1972-12

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Jaget, Charles William

Monterey, Calif. : Naval Postgraduate School

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Charles William Jaget

NAVAL POSTGRADUATE SCHOOL
Monterey, California

THESIS

THE GROWTH OF IRON WHISKERS
BY THE HIGH TEMPERATURE REDUCTION
OF FERROUS HALIDE SALTS

by

Charles William Jaget

Thesis Advisor: W. M. Tolles

December 1972

The Growth of Iron Whiskers by the High Temperature Reduction of Ferrous Halide Salts

by

Charles William Jaget
Lieutenant, United States Navy

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

NAVAL POSTGRADUATE SCHOOL

ABSTRACT

The growth mechanism of iron whiskers produced by the hydrogen reduction of iron halide salts was investigated by the variation of a number of parameters. The observations are correlated with current theories and with the thermodynamic behavior of this reaction which indicates that the tip of the growing whisker should be colder than the ambient medium (the cold tip). The mass growth of iron whiskers in the presence of carbon was examined to evaluate the potential of this method to produce marketable whiskers. An unidentified, non-metallic whisker growth was discovered growing in bone charcoal. Growth was determined to require the presence of a ferrous halide and calcium orthophosphate. Further postulates concerning the cool tip theory are made.

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23. Base of whisker clump exhibiting encrusted bases and tips when He flow is substituted for H_2 flow three minutes prior to removal from furnace, exp. 120.

I. INTRODUCTION

A whisker is a single, nearly perfect crystal of an element or compound which dimensionally would class it as a fiber. For the purpose of this thesis a crystal which is at least ten times as long as its mean diameter will be considered a whisker. This thesis reports observations almost exclusively for iron whiskers produced by the hydrogen reduction of iron halides at temperatures around $1000^{\circ}K$.

Whiskers have been observed as early as the 16th century as hair-like growth emerging from copper and silver sulfide ores. The cotton-like silver fibers (Haarsilber) produced by the reduction or oxidation of silver sulfide puzzled scientists for several centuries. In 1956, Brenner (Ref. 1) reported the conditions and the methods used for the growth of Fe, Cu, Ag, Ni, Co, Pt, and Au whiskers by the reduction of their halide salts. Many compounds such as Al_2O_3, SiC, and B_4C also can be grown as whiskers.

The impetus behind current whisker research lies in the fact that whiskers are the strongest forms of solids yet discovered. Their strength approaches the theoretical cohesive strength of solid matter. High-strength whiskers have great potential as strengthening agents in composite materials. Composites of plastics and metals utilizing the fascinating properties of whiskers could produce engineering materials several times the strength and flexibility of present composites. Continued developments are expected to greatly reduce the present high cost of producing some types of whiskers.

Metallic whiskers produced by the hydrogen reduction of their halide salts are in general of poor quality, low yield compared to that

theoretically possible and difficult to separate from the substrate on which they grow. Tests on selected specimens have produced the impressive strength noted earlier. Improvement of the general quality has been difficult as the growth mechanism is not fully understood.

The cool tip mechanism was proposed by Hovermale (Ref. 7) as a possible mechanism. The proposal is a new direction in whisker growth thought. Based on reaction thermodynamics and heat flow modeling the proposal may prove useful in examining the method of whisker growth.

The thrust of this thesis is to uncover experimental evidence which will support or refute this theory. An accurate mechanistic picture of the growth process and nucleation mechanism will enable growing technique refinements which will produce longer, stronger, useable iron whiskers.

II. BACKGROUND OF EXPERIMENTAL OBSERVATIONS AND THEORIES OF WHISKER GROWTH

A. EXPERIMENTAL LITERATURE OBSERVATIONS CONCERNING THE GROWTH OF IRON WHISKERS.

1. Reduction Without Carbon Present.

The reduction of halides without carbon present has been the most widely used method of iron whisker production. By varying the conditions under which the reduction takes place researchers have greatly altered whisker growth. Parameters varied included temperature, H_2 flow rate, amount of material present, size of chamber, purity of materials and effect of specific impurities.

a. General Observations

The hydrogen reduction of halide salts is a very inefficient process with present experimental techniques for the conversion of iron into small diameter filaments. The bulk of the halide is reduced to iron which remains in the bottom and on the sides of the boat. This iron is in the form of small particles and/or a continuous skin or foil depending on conditions and location in the boat. In general, the whiskers remaining at the completion of a reduction grow from the sides of the reaction boat toward the center of the boat. The growth generally takes place only in a narrow band at the interface of the melt and the boat. Often whiskers are clumped and appear to grow from a common base. The number and size of the whiskers will depend on the growth conditions employed but for a given set of conditions greater quantities of halide in larger boats produce larger whiskers of greater diameter. Increasing only the quantity of halide reduced will increase the average whisker diameter but will not significantly increase the number of whiskers.

The strongest iron whiskers which have been produced grow with a [100] fiber growth axis. Two other growth axes are also commonly observed; the [111] and the [110]. Figure 1 shows the external shapes associated with the different fiber axes. Impurities and/or nucleation sites appear to determine the fiber axis orientation.

b. Observations Concerning Impurities

The alteration of the amount and type of impurities present in the melt greatly alters whisker growth. Gorsuch [Ref. 4] reports that impurities are somehow responsible for whisker growth. Small irregular shaped iron particles, rather than whiskers, were produced when high purity iron halide salts were reduced in dry hydrogen (-60° F dew point or lower) and these impurities influence both the nucleation and growth processes.

Iron oxide, Fe_2O_3 is a common impurity. Its addition to commercially available iron halides reduced in a hydrogen atmosphere produced whiskers with a [100] fiber axis. Those produced from the halide alone had a [111] fiber axis [Ref. 4]. The average diameter of the whiskers tends to decrease as the impurity content increases.

Impurities can also be added to the reducing gas. Their general effect is to reduce the average diameter, except for inert gases which have no effect. Sufficient quantities of impurity gas will cause whisker growth to cease. The presence of water vapor appears to assist the reduction of halides in the presence of Fe_2O_3. Increasing the moisture content was found [Ref. 4] to progressively reduce the rate of evaporation and the rate of reduction of the halide salt. It has also been shown to increase the tendency for the liquid halide salt to wet the surface of an iron boat.

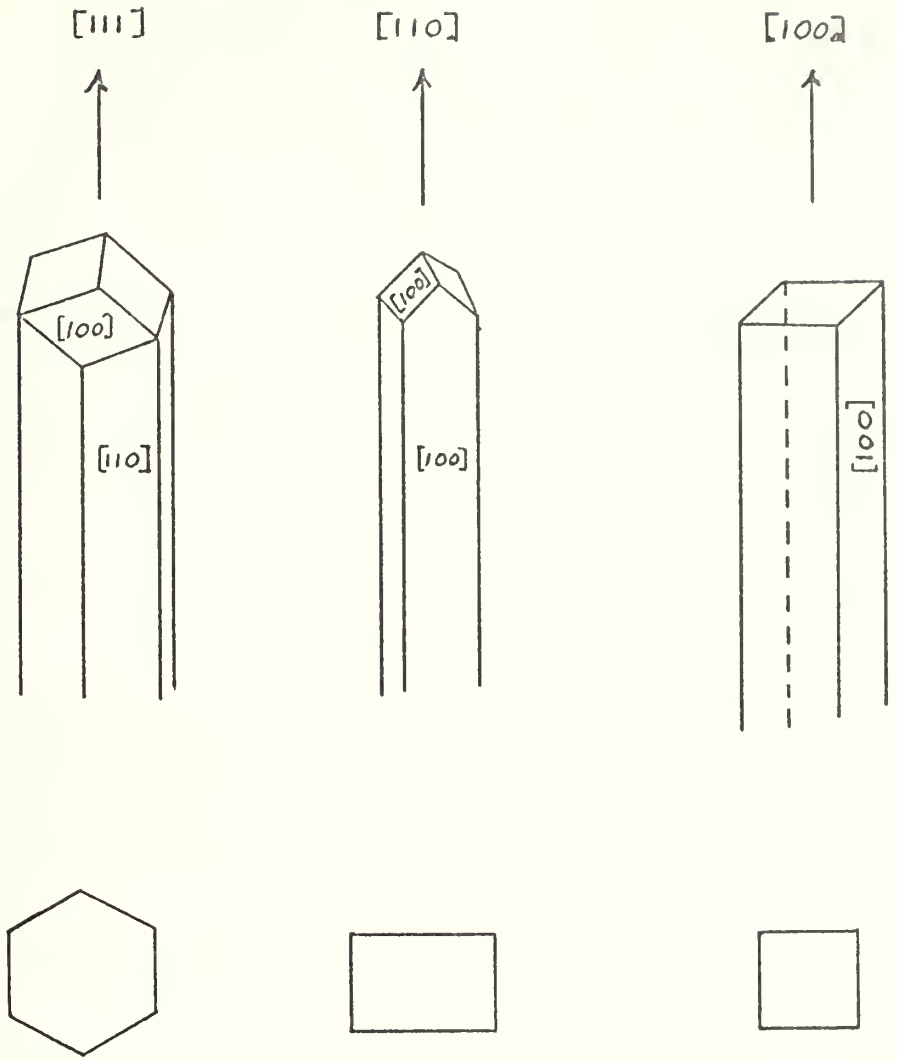

FIGURE 1. Schematic diagram of the dependence between shape of the whisker tip, the direction of growth and the cross section.

c. Observations Concerning Temperature

For each halide salt there exists an optimum temperature ange for best whisker growth. As the temperature increases the taper f the whisker increases and the whiskers are more frequently kinked nd distorted. As the temperature is reduced from the optimum the size nd number of whiskers decrease until the melting point is reached at nich point all growth ceases.

d. Observations Concerning Hydrogen Flow Rate

Hydrogen flow rate above a minimal velocity has little influence on the tendency for whisker growth. At high flow velocities owever, the whiskers become badly kinked and distorted.

. GROWTH THEORIES

1. Screw Dislocation Theory

Two dimensional nucleation in the gas phase requires large upersaturations on the order of 1.5 to 10. Early experiments revealed nat crystal growth on already formed crystals proceeded even when the upersaturation ratios were on the order of 1.01. F. C. Frank [Ref. 3] roposed that the crystals did not have smooth growth surfaces but rather the growth surfaces contained dislocations. These dislocations form "screw" and the crystal face always has exposed molecular terraces on hich growth can continue. The need for fresh two dimensional nucleaions never arises and the crystal face can grow perpetually at low alues of supersaturation. Each new molecular layer faithfully reproduces the original dislocation. Growth would continue on the face containing the dislocation indefinitely.

The existence of screw dislocations in metallic whiskers grown y the reduction of metal halides has neither been proved or disproved.

the vapor-solid surface the deposition site for the whisker forming material. The presence of a liquid layer in contact with the growing crystal has important consequences. The surface of the liquid has a large accomodation coefficient and therefore is the preferred site for the deposition of the product material. As the product material enters the liquid from the liquid-vapor surface the liquid becomes supersaturated with the whisker forming material and precipitation occurs at the solid-liquid interface resulting in crystal growth along one direction. An idealized drawing of the VLS mechanism is illustrated in Figure 2 for a silicon crystal using gold as the impurity. For silicon the reduction of $SiCl_4$ with hydrogen or the disproportionation of SiI_2 to produce Si does not take place in the vapor phase. The author of reference 9 reported experimental evidence indicating that the process is a heterogeneous surface-catalyzed reaction occuring at the liquid surface.

For a condensation reaction α is the fraction of impinging atoms which become accomodated (adsorbed) on an extensive crystal surface. Theory predicts that the value of α depends on the state of perfection of the surface and on σ, the degree of supersaturation. The growth rate of a crystal is proportional to the product $\alpha\sigma$. For a given σ the more imperfect the surface the lower is the supersaturation required to get surface adsorption. Figure 3 is a modification of a graph found in reference 9, pg. 62. It depicts the relative growth rate for an imperfect crystal (one that contains a screw dislocation), a perfect crystal surface, and a surface of unit accomodation coefficient (clean liquid). For the first two cases, the growth rate is essentially zero below a critical supersaturation (σ_1, or σ_2, respectively) and increases to the ideal rate with increasing σ. Nucleation of new layers, within the

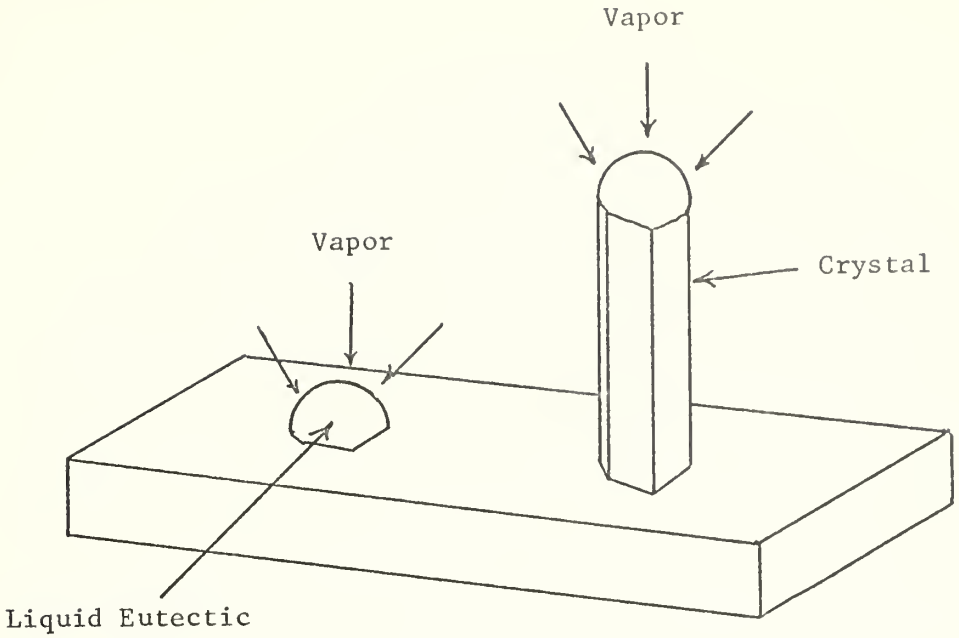

Figure 2. Idealized Drawing of VLS Mechanism

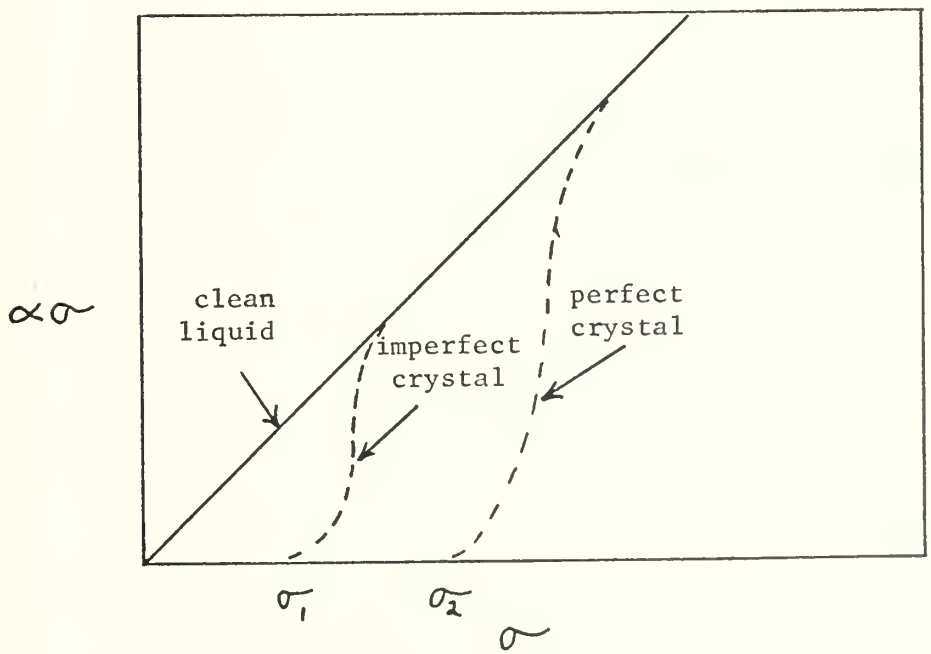

Figure 3. Relative Growth Rates of Crystals Based on the Type of Exposed Surface

respective ranges of supersaturation, occurs either by two dimensional nucleation on the perfect surface or through the agency of an emergent screw dislocation on the imperfect one. The straight line depicts the relative growth rate for a clean liquid surface (ideal rate). A clean, liquid surface is distinctly different from that of a perfect, or imperfect crystal surface and can be considered as ideally "rough." The liquid surface is composed of ledges and steps only interatomic distances apart. Accomodation sites exist over the entire area. Deposition on a liquid surface, therefore, follows the ideal rate depicted in figure 3 and is the basis for growth by the VLS technique occuring as a result of the presence of liquid forming impurities.

The prediction of figure 3 holds strictly for evaporation - condensation and the homogeneous vapor-phase reaction. For a heterogeneous reaction, the presence of the liquid droplet in the reaction region can have additional effects. The large accomodation coefficient results in a long "stay time" of adsorbed gas molecules at the liquid surface. Furthermore, the impurity which forms the liquid may also function as a reaction catalyst for the heterogeneous reaction. Each factor results in an enhanced deposition rate on the liquid.

The VLS growth process is a two step process. After the formation of the liquid a fast initial extension in length occurs by addition of material at the tip of the whisker. This is followed by a slow increase in thickness (layer growth). The leader is virtually uniform in cross section from base to tip. Subsequent growth is not always uniform.

By understanding this mechanism great strides have been made toward the production of useable whiskers which grow by this method.

3. Cold Tip Theory

The Cold Tip Theory was postulated by Mark Hovermale in his master's thesis in June of 1972 [Ref. 7]. For the reaction:

$$FeCl_2 + H_2\ (g) \rightarrow \underset{\text{(whiskers)}}{Fe\ (s)} + 2HCl\ (g)$$

proceeding at 1000°K, his analysis of the thermodynamics using the values tabulated in reference 11 determined that:

(1) If $FeCl_2$ is a gas the reaction is exothermic by approximately 6,000 calories per mole.

(2) If $FeCl_2$ is a liquid the reaction is endothermic by approximately 24,000 calories per mole.

(3) If the reaction proceeded at a location other than the tip with subsequent migration of the Fe atom the reaction at the growth site would be exothermic due to the heat of crystallization of Fe.

References 2 and 10 report that for the metal halides, hydrogen reduction in the gas phase followed by the deposition of the metal atoms in a crystal lattice cannot support the growth rates experienced experimentally; rather they propose it is more likely that the metal halide vapor diffuses to the metal surface where it is reduced. The metal atoms produced then diffuse to a growth site.

If the reactants were liquid the loss of heat resulting from the reduction occurring at the tip would result in the tip becoming cold relative to its surroundings. Hovermale [Ref. 7] constructed a computer model of heat flow at a whisker tip. This model treated the dynamic heat-flow equations for a whisker tip in which heat was continually being removed at a constant rate per unit area of surface. The results quantitatively verify that the region of highest curvature is the region of greatest temperature differential. That is, the tip of the whisker would have a lower temperature than any other portion of the whisker.

In addition, a thermal gradient would be established from the tip to the base of the whisker from ordinary heat flow considerations. This too, favors a cool tip. Further, the flux of liquid from the base of the whisker to the tip performs a sweeping action, tending to maintain the tip at a still lower temperature. All three of these effects favor the cool tip provided that the liquid flux from the bottom is the major source of $FeCl_2$ to the tip.

The cold tip mechanism can be summarized as follows:

(a) The initial halide to be reduced is provided by liquid from the melt.

(b) Growth is initiated by a nucleating site on the substrate. This site need not be a cold area but could be a screw dislocation, a radius of curvature or a preferential nucleation site.

(c) As a whisker develops initially, reduceable halide is provided by liquid flowing up the sides of the whisker from the melt. The tip becomes cold and the growth is rapid.

(d) An intermediate period of growth occurs as a thermal equilibrium is reached between the endothermic reaction and the exothermic condensation.

(e) Growth is terminated when the atmosphere is less than saturated with halide vapor and vaporization of the liquid at the tip occurs faster than it is supplied. This termination situation would occur when the whisker has grown above the halide vapor or when the starting material became depleted.

C. DESCRIPTION OF IMPORTANT REACTANT MATERIALS

The reactants usually involved in the production of iron whiskers are $FeCl_2$, $FeBr_2$, $FeCl_3$, and Fe_2O_3. Reference 4 reports the following facts about these reactants:

Ferrous chloride, $FeCl_2$, has a density of 2.98 g/cm^3 and melts at 670-674°C. No thermal dissociation at temperatures up to 1000°C has been noted, but there is evidence that some $FeCl_3$ may be formed by partial decomposition. It reacts with oxygen and water vapor in the temperature range of interest to form various types of iron oxides such as α-Fe_2O_3 and Fe_3O_4. The commercially available $FeCl_2$ is the tetrahydrate $FeCl_2 \cdot 4H_2O$. Upon melting, this material forms anhydrous $FeCl_2$ and some ferrous oxychloride. Relatively high purity material can be obtained in an HCl atmosphere or by hydrogen reduction of high purity $FeCl_3$.

Ferrous bromide, $FeBr_2$, has a density of 4.636 g/cm^3, and melts at 684°C. Heating in air at temperatures up to approximately 310°C or in an atmosphere containing significant quantities of water vapor at 500°C or higher results in the decomposition of $FeBr_2$ to α-Fe_2O_3.

Ferric chloride, $FeCl_3$, melts at approximately 300°C and boils at approximately 310°C. The $FeCl_3$ vapor which exists as the dimer, Fe_2Cl_6, at low temperatures is rapidly reduced to $FeCl_2$ in hydrogen at temperatures of 350°C and above.

Ferric oxide, α-Fe_2O_3, is reduced rapidly in hydrogen at 500°C and above to Fe_3O_4, FeO, and finally to α-Fe. During reduction the oxygen ions are maintained with a close-packed structure but the iron ions are rearranged in various ways so that a different crystal structure results for each oxide.

III. EXPERIMENTAL

A. EXPERIMENTAL PROCEDURE AND APPARATUS

The apparatus used for growing whiskers is shown diagramatically in Figure 4. It is almost identical to the apparatus used by Brenner in 1956 [Ref. 1]. The quartz tube was 29 mm O.D., 26 mm I. D. and 120 cm long. The quartz boats were made of 19 mm O.D., 17 mm I. D. quartz about 10.5 cm long. The metal liners were made from 28 gauge galvanized steel. After forming, the zinc coating was removed with HCl and the clean liners were stored in acetone until just before they were used.

The chemicals used in these experiments were standard commercial reagents. A complete list is included in Appendix A. The $FeCl_2 \cdot 4H_2O$, $FeCl_2$, $FeBr_2$, and NH_4Br were ground in a mortar and pestal prior to use except where noted.

The general procedure used for conducting a typical reduction experiment follows:

(1) The steel liner was placed in a quartz boat and the reactants added.

(2) The loaded boat was placed in the cooling section of the quartz reaction tube.

(3) The tungsten rod was attached to the boat and the stopper inserted. Helium gas was admitted at a rate of 1.0 cubic foot per hour (CFH) for ten minutes to flush the oxygen-containing atmosphere from the tube prior to admitting hydrogen. On subsequent runs when the oxygen content of the atmosphere in the tube was assumed low due to the short period of time the tube was unstoppered, the purging time was reduced to three minutes.

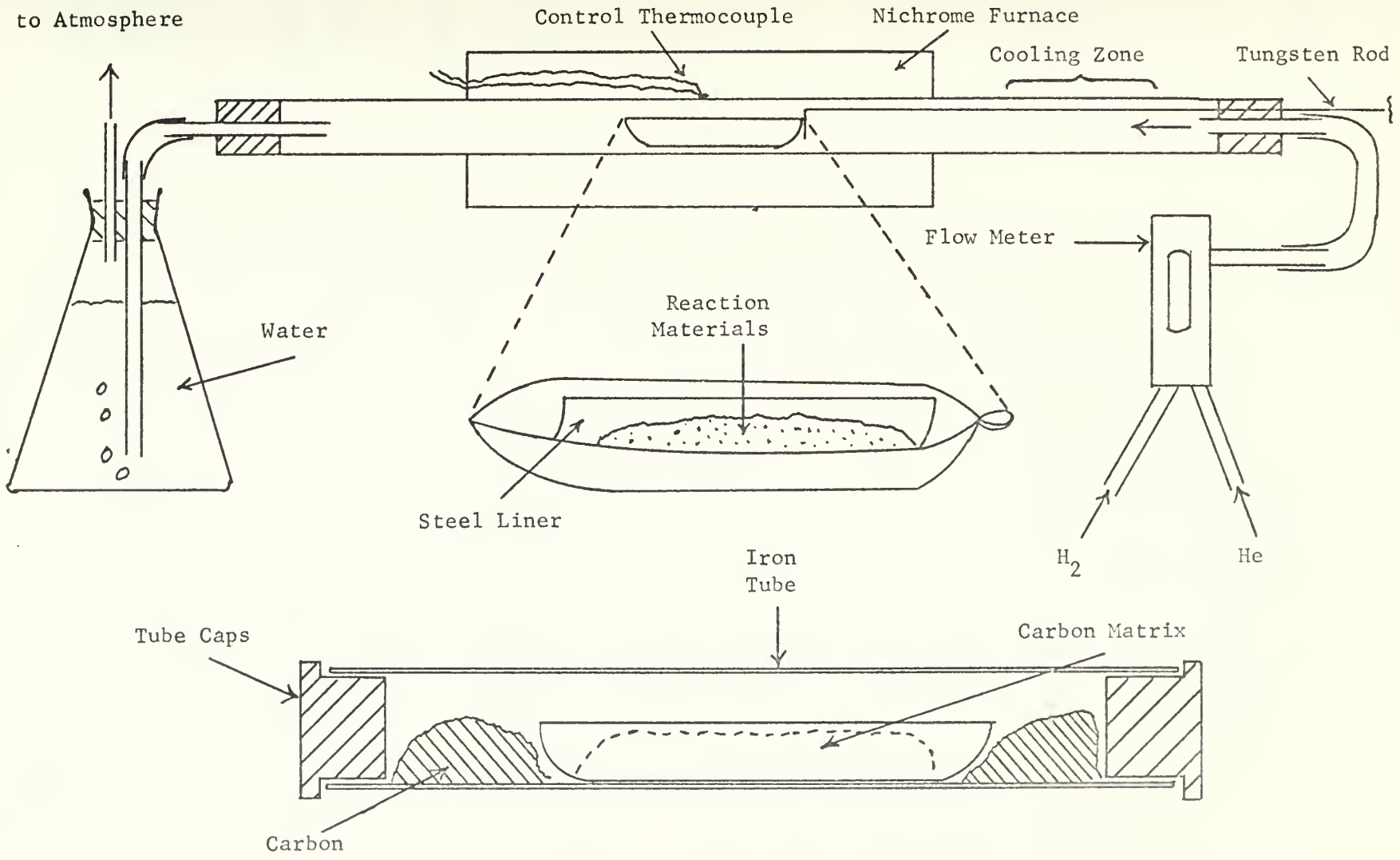

Figure 4. Apparatus for Growth of Whiskers

(4) The hydrogen flow was started when the helium flush was complete. Hydrogen was flushed through the tube for three minutes at 0.6 CFH.

(5) The hydrogen flow was then adjusted to the desired rate for the reduction and the sample was pushed into the hot zone with the tungsten rod, where the reduction reaction: $FeX_n + \frac{n}{2}H_2 \rightarrow Fe + nHX$ proceeded. When the sample had remained for the desired time period it was withdrawn to the cooling section, the hydrogen flow was stopped and the helium flow was started.

(6) The sample was removed after about two minutes in the cooling section and another boat was placed inside and the process repeated.

Large yields of iron whiskers have been achieved by the reduction of iron halides in the presence of carbon black [Ref. 8]. The atmosphere for such growth can be either hydrogen or a charcoal-air system. The charcoal-air system produces hydrogen by the reaction:

$$H_2O + C \rightarrow H_2 + CO$$

The hydrogen is needed in the reducing atmosphere but the CO is not. The water needed is provided by moisture in the charcoal blocks. The apparatus is shown in Figure 4.

The reaction products were examined with a bench top stereo microscope. When greater magnification was desired the examination was conducted with a Zeiss microscope. All such examinations were made using dark field objectives. Magnification ranges from 40 to 1280 times were available with this microscope. Color slides were taken with good results using the installed camera, Kodachrome II film (ASA-25) and an 80A filter to correct the color.

B. EXPERIMENTS WITH $FeCl_3$ MIXTURES

1. General

The first experiments conducted revealed that fresh, green $FeCl_2 \cdot 4H_2O$ from new bottles produced far fewer whiskers than the same material obtained from old bottles. The old bottles contained $FeCl_2 \cdot 4H_2O$ which was partially oxidized by contact with air. This material was light yellow when ground as opposed to the light green material from the new bottles. The addition of $FeCl_3$, and Fe_2O_3 to the fresh $FeCl_2 \cdot 4H_2O$ was intended to reproduce the composition of the material in the old bottles.

2. Experimental

A 60:40 mixture (by weight) of $FeCl_2 \cdot 4H_2O/FeCl_3 \cdot 6H_2O$ produced a fair number of poor quality whiskers, exp. 8. The addition of ferric oxide to form a 60:30:10 mixture of $FeCl_2 \cdot 4H_2O/FeCl_3 \cdot 6H_2O/Fe_2O_3$, exp. 9, produced a fair growth equivalent to that resulting when the old material was used. The whiskers were encrusted with unreduced halide. Figure 5 is a picture of two of the whisker tips from this experiment. The shape of the halide at tip is characteristic of the shapes seen in most later experiments regardless of the reactants. Two more experiments were conducted using a three reactant mixture however, $FeCl_2 \cdot 4H_2O/ Fe_2O_3$ mixtures produced more and better whiskers than three reactant mixtures.

3. Conclusions

The Fe_2O_3 produced as the $FeCl_2 \cdot 4H_2O$ is air oxidized was responsible for the superior growth when old materials were used. The whiskers produced with $FeCl_3 \cdot 6H_2O$ present could be easily scraped from the liner by soaking for five minutes in HCl or boiling water after air oxidation

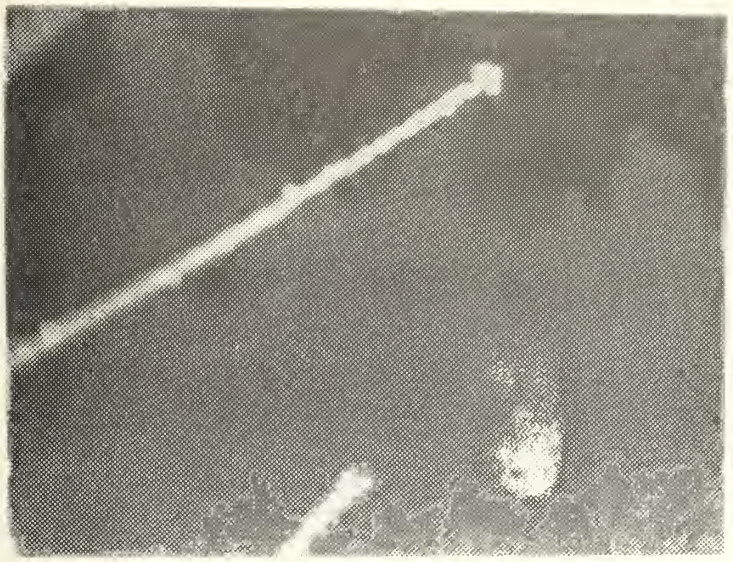

Figure 5. Coating of Halide on Whisker Tip. Note Shape of Halide at tip. Exp. 9

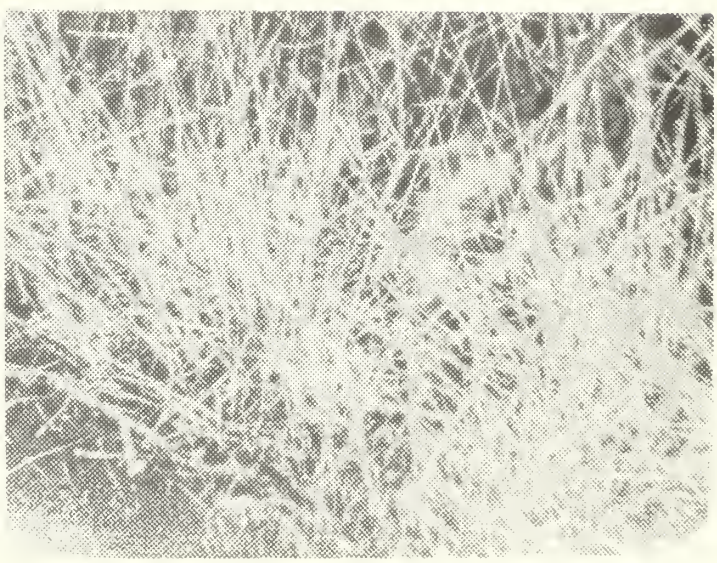

Figure 6. Crop of whiskers grown with 7:11 mix in a standard boat. All whiskers are encrusted with yellow salt-like material. Close examination will reveal bulbous shapes at the ends and globules attached to the sides. Exp. 21. Magnification 15X.

had turned the foil at the base of the whiskers brown. This appeared to be due to the expansion of the relatively large quantity of unreduced salt remaining intimately mixed with the foil as it regained its water of hydration from the atmosphere.

C. EXPERIMENTS WITH 7:11 MIX

1. Background

Hovermale [Ref. 7] reported excellent yields of iron whiskers obtained by the reduction of a mixture of Fe_2O_3 and NH_4Br. The optimum ratio was determined to be 7.0 g Fe_2O_3 to 11.0 g NH_4Br for reduction at 730°C. This mixture was referred to as the 7:11 mix. The reaction is believed to proceed by a two-step reduction:

$$H_2 + 4NH_4Br + Fe_2O_3 \rightarrow 4NH_3 + 2FeBr_2 + 3H_2O$$

$$FeBr_2 + H_2 \rightarrow Fe + 2HBr$$

2. Experimental Procedure

Between 2.5 and 3 grams of 7:11 mix were placed in each lined, quartz boat and reduced at 730°C for ten minutes. In three experiments steel thumb tacks were imbedded on their heads in the reaction mixture to examine the possible effect of increasing the radius of curvature. The points were cut from some of the tacks to produce sharp edges. The hydrogen flow rate was 0.15 CFH for experiments without tacks and 0.3 CFH for experiments with tacks.

3. Observations

The yield of whiskers produced by this mixture was much greater than that produced by other non-carbon containing mixes. Figure 6 is a picture of a typical boat. The whiskers grow from the edge of the melt with their axes predominately horizontal and toward the center of the

boat. They were generally thin, straight (compared to other methods), slightly tapered and of various lengths. Many were longer than a centimeter and some bridged from side to side. Many had a yellowish salt crust adhering to their sides which became thicker and was most often present at the tip. The salt at the tip was lumpy, flat on top and basically square.

When removed from the reaction furnace after reduction the bottom of the boat including the base of the whiskers was covered with metallic foil. Whisker removal was difficult as the filaments adhere strongly to this foil.

Whiskers grew radially from the tacks in the same manner as from the sides. Metallic foil always covered the base on which they grew. Very little could be determined about the effect of a small radius of curvature as the growth was too prolific where the conditions were right, i.e. at the narrow band near the edge of the melt. Figure 7 shows the tip of a tack which was in the growth zone. Figure 8 is a picture of the tip of one of the whiskers growing on the tip of the tack.

D. EXPERIMENTS WITH A CARBON MATRIX

1. Iron Whiskers

a. Background

The mass growth of iron whiskers reported in reference 8 prompted examination of this medium using the 7:11 mixture discussed in the preceding section. The goal was to produce straight, strong, separable whiskers in high yield which could easily be removed from the growth matrix. The carbon containing filaments produced by the reduction reactions is referred to as a matrix. Different types of carbon

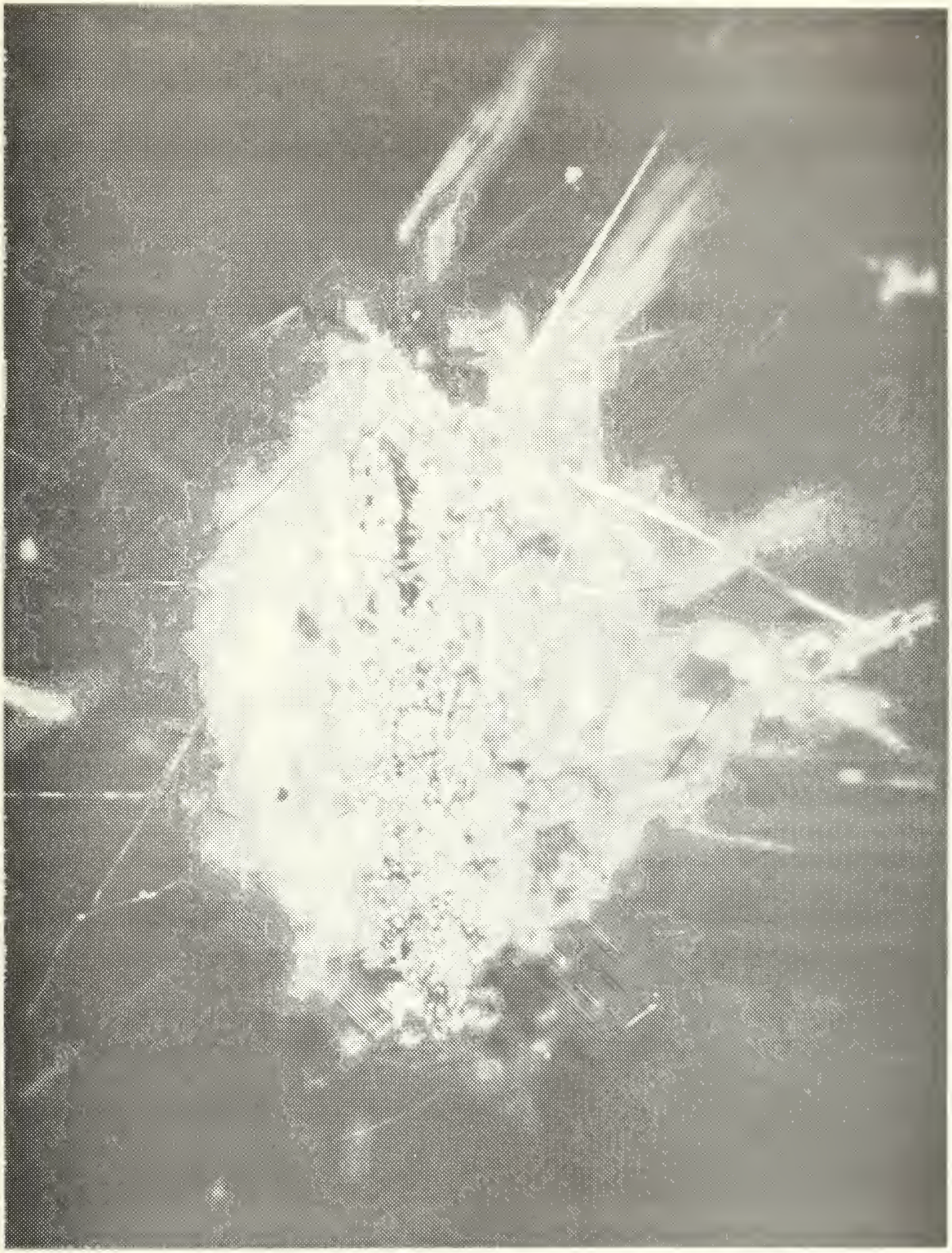

Figure 7. Tip of tack used in experiment 45. Note foil on which whiskers grow, some balls at tip and bent, distorted whiskers. Magnification 40X, enlargement 6.4X (256X)

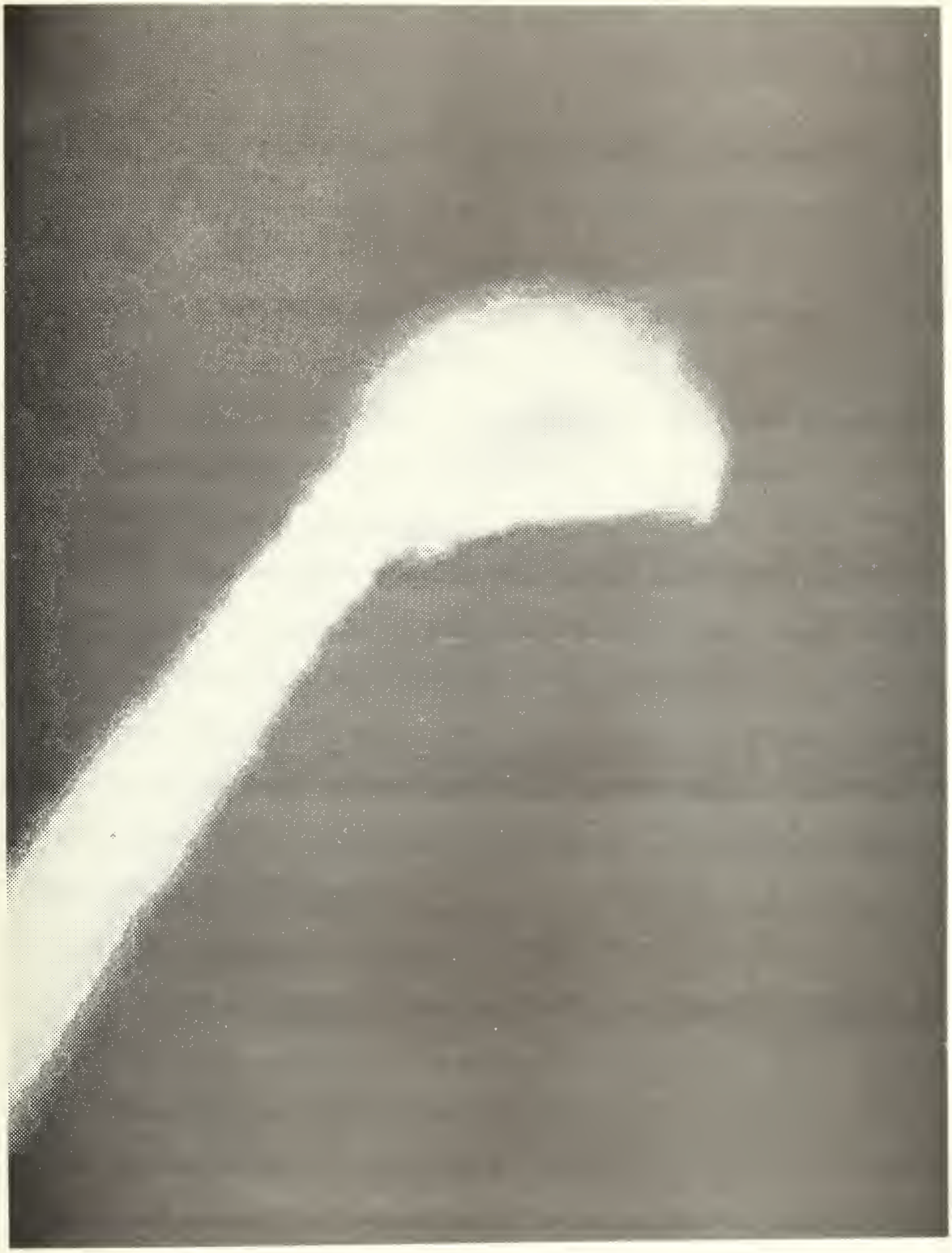

Figure 8. Tip of whisker which grew on tack in exp. 45. Note amount of halide at tip and encrusted stem. Magnification 160X, enlargement 6.4X (1024X)

were examined to empirically determine if different effects would be noted and to optimize the resulting growth toward the goal.

b. Experimental Procedure

The 7:11 mix and the selected carbon were weighed, mixed and placed in unlined quartz boats. The amounts, reaction times, H_2 flow and abbreviated observations for these experiments are tabulated in Table I. Besides varying the types of charcoal, mixture ratios were altered to optimize growth and determine growth limits. Samples of identical mixtures and quantities were reduced for short periods to allow observations and comparisons of the initial growth.

c. General Observations

The whiskers grown by this method were short, very fine, bent, tangled and most often branched. Attempts to separate the whiskers using an ethanol wash and magnetic separation succeeded in separating the iron whiskers from most of the carbon but the resulting tangled mass resembled steel wool and was judged unmanageable. There was very little metallic foil produced by this method and most of the iron is believed to form filaments.

d. Specific Observations

(1) Norit A. The weight of carbon present was less than that of the 7:11 mix used. The whiskers produced were small diameter filaments with generally a metallic bulb or foil at the tip. Foil covering the bottom of the boat was also produced as a major product of the reduction. The whiskers grew on the surface of the foil as opposed to being contained within a carbon matrix.

(2) Lamp Black. Only one experiment was conducted using lamp black and the 7:11 mix. The whiskers produced were contained

within the matrix were clumped and tangled in the manner described in Reference 8. Since separation for use did not appear feasible, further experiments were not attempted with this medium.

(3) Bone Charcoal. Bone charcoal produced great masses of small, tangled, branched whiskers within the matrix when the 7:11 mix/bone charcoal ratio was about 50:50. The matrix was soft and powder-like. The number of whiskers produced was greatly reduced when the percentage of 7:11 mix dropped below 20% and non-existent below 10%. The number diminished rapidly as the percentage of 7:11 mix approached 75%.

Most filaments were encrusted with a yellow salt which dissolved in water. They were firmly affixed to a carbon particle at one end and the tip extended into the spaces between particles. The covered filaments were definitely iron as they were magnetic. Other filaments were present which were straight and generally had a ball at the growth (tip) end. Figures 9 and 10 show examples of these filaments. Though it cannot be proved conclusively that these particular whiskers were not iron, later experiments indicated that a similar material was non-magnetic, and hence not iron.

The filament in Figure 10 was firmly attached to the carbon on which it grew. It appears to have grown without direction at first before it established an unvarying crystal structure. The stem is shiny and the bulb at the tip is yellow. The droplets clinging to the sides are clear. Figure 9 is a picture of a whisker similar to the one shown in figure 10. The lower portion of this filament cannot be seen because of the limited depth of field at this magnification which prevented seeing the entire filament at one time. The

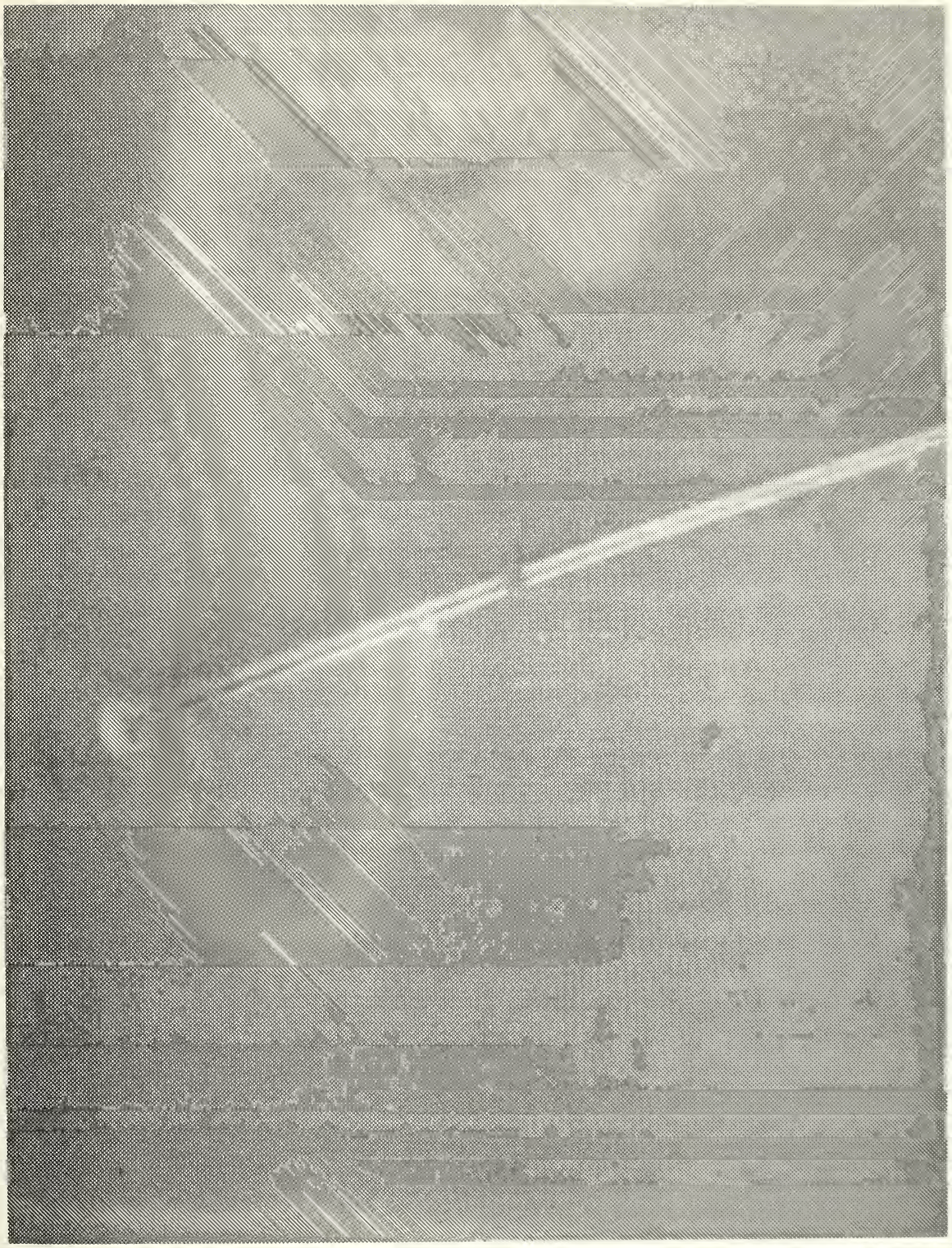

Figure 9. Single whisker isolated on glass slide from exp. 35. Note the ball at the end, globules adhering to the sides and the hollow appearing stem. Magnification 1024X, enlargement 6.4X. (6554X)

Figure 10. Single whisker attached to carbon particle, exp. 36. Note shape of tip, early growth pattern, globules attached to the whisker sides and solid stem. Magnification 800X, enlargement 6.4X (5120X)

base looked like the stem except for two "leaves" of yellow salt springing from the base.

Mixtures were reduced for short periods of time to examine early growth. It was hoped that by stopping growth early, small but untangled, and therefore separable, whiskers would result. Examination of the resulting matrix showed that most of the filaments formed and grew within the first five minutes and very little change occurred after that. The first filaments began appearing after the boat had been inserted into the hot zone for 45 seconds. The filaments obtained with less than five minutes of reduction were heavily encrusted with a lumpy, yellow salt covering. The shape, size, branching, etc., of the supporting filament could not readily be determined. Dissolving the yellow salt in water revealed very thin, shiny filaments which were always bent and branched. These filaments did not separate from the carbon with water. Many clear filaments, as previously described were also present. They were generally straight and had balls at their tips. These filaments were not covered with salt even at short heating times.

Reduction of the amount of 7:11 mix present to 10% by weight resulted in no filamentary growth. However, the carbon became covered with tiny buds. Figure 11 shows this bud-like growth.

e. Conclusions

Bone charcoal produced the most prolific filament growth. However, most of the filaments were branched, tangled and bent. The everpresent, thick covering of salt may indicate that the filaments grow in a liquid. It is not known what proportion of the filaments produced with bone charcoal and 7:11 mix were not iron. The next section will describe the investigation of the clear, non-magnetic filaments

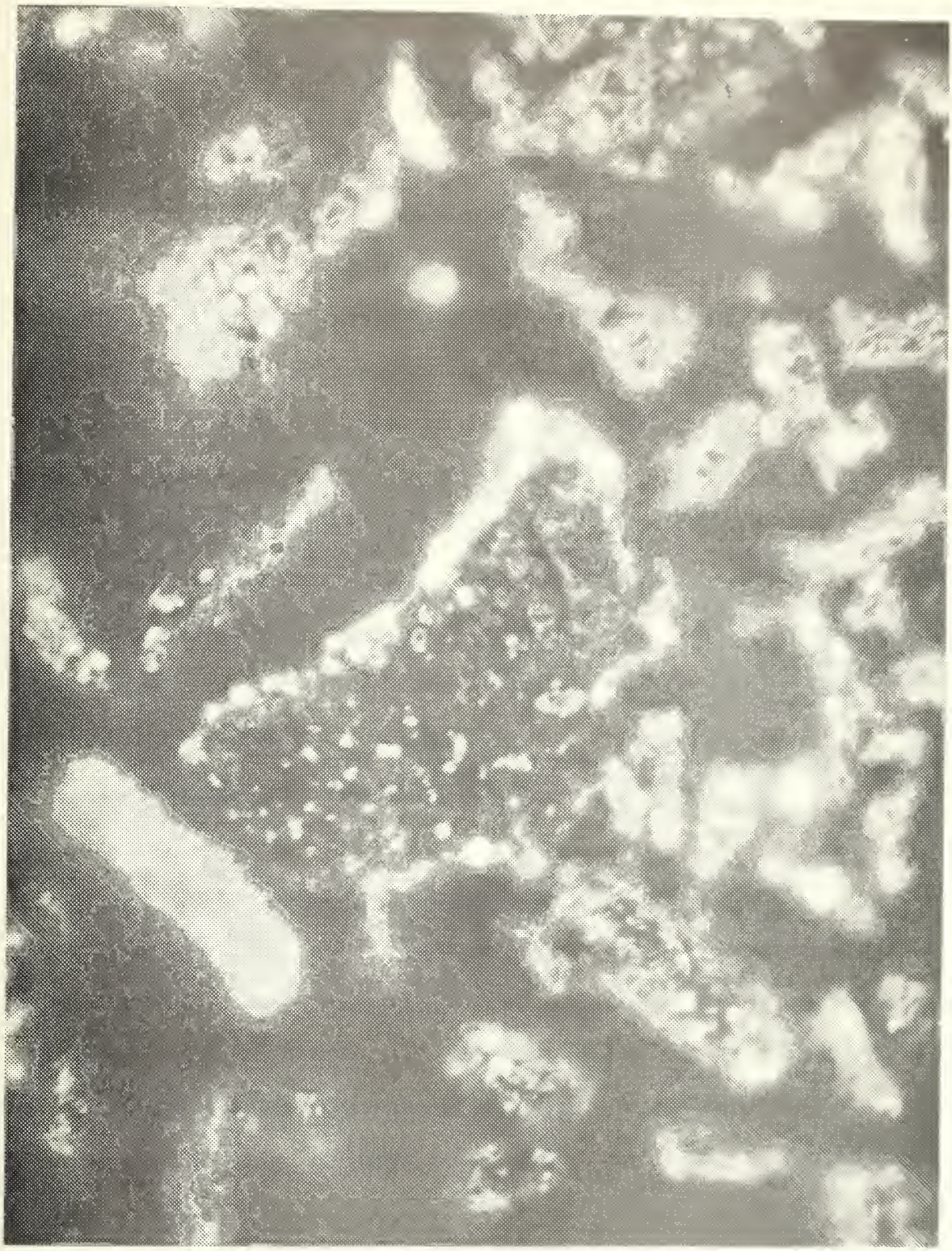

Figure 11. Large flat carbon particle showing bud-like growth at edges, exp. 51. Magnification 400X, enlargement 6.4X. (2560X)

found only when bone charcoal was used in conjunction with a halide reduction. The existence of other than iron whiskers negates the use of observations made with a bone charcoal medium to support mechanistic arguments for the growth of iron whiskers.

The high yield growth associated with carbon is very encouraging and further experimentation may yield a production scheme, though none was found in these experiments. The metallic or foil-like balls seen at the tip when Norit A was present but not when the 7:11 mix alone was reduced indicates a mechanistic change or modification. Kittaka and Kaneko [Ref. 8] reported that particles of carbon act as a strong sink for halide and allowed for growth at the tip by vapor transport. They proposed that the foreign particles are larger in size than the whisker diameter and cover the entire growth step. The halide is condensed on the carbon, reduced in the liquid form and the iron atom migrates to the growth step (screw dislocation).

2. Non-Magnetic Filaments

a. General

The boat for the experiment 47 was loaded with a mound of 7:11 mix in the forward portion of the boat and a mound of bone charcoal in the after portion of the boat. After reduction the surface of the bone charcoal nearest the 7:11 mix was covered with a white frost. Microscopic examination revealed the frost consisted of white of clear crystals. Addition of water to a surface sample of the carbon revealed many very small, shiny, freely floating filaments, small enough to show brownian motion. The tiny filaments were thought to be iron but they did not orient in a magnetic field. The experiment was repeated with identical results. The experiments conducted to examine this whisker are tabulated in Table II.

b. Determination of Growth Requirements

The vapor transport of reactants required in exp. 47 limited the possible reactants to bone charcoal, NH_4Br and $FeBr_2$, or a combination of any two or all three.

The bone charcoal of exp. 47 was replaced by piles of lamp black, Norit A, and graphite powder without producing filaments, implying that bone charcoal was required. A 50:50 mixture of $FeBr_2$ and NH_4Br was mixed individually with the carbons mentioned above. Many extremely fine, straight, long, non-magnetic (NM) filaments were found in the bone charcoal mixture but none were found with the other carbons. A cursory search of ref. 5 revealed that bone charcoal is composed of carbon and $Ca_3(PO_4)_2$. The possibility that calcium phosphate was responsible for the NM filaments existed.

It was discovered that previous experiments at this school had also produced NM filaments using bone charcoal. The most successful method was to mix 2g $FeCl_2$, 2g bone charcoal and 0.5g silicic acid and reduce the mixture in an iron tube. The silicic acid, $SiO_2 \cdot XH_2O$, was present ostensibly to slowly provide water which would react with the carbon to produce hydrogen. The iron tube was small enough to slide into the quartz tube. Loose fitting plugs closed off the tube ends. The boat was placed in the center of the tube and charcoal was piled at each end. The caps were inserted and the tube pushed into the furnace which was left open to the atmosphere. A diagram of loaded iron tube is part of figure 4. The tube remained in the furnace for 8 to 20 hours. Experiment 69 duplicated this procedure and produced a tremendous yield of clear NM filaments which were longer and of larger diameter than those

previously produced. Figures 12 and 13 are photographs of the high yield produced in exp. 69 and exp. 82, respectively.

To investigate the functions of the calcium phosphate a boat was prepared containing four separate piles. Three piles were a mixture of 0.3g $Ca_3(PO_4)_2$, 0.6g $FeCl_2 \cdot 4H_2O$ and 1g of either bone charcoal, Norit A, or lamp black. The fourth pile contained only calcium phosphate and ferrous chloride. The boat was placed in an iron tube and heated for 15.5 hours. All four piles produced NM filaments (exp. 70). The NM filaments were concluded to be a combination of a ferrous halide and calcium phosphate.

Additional experiments were conducted to optimize the yield to allow for separation and probable identification. The method used in experiment 69 proved to be the most successful, however, the silicic acid posed an additional separation problem. Similar experiments with the silicic acid inside the iron tube but not intimately mixed with the reactants were much less successful even with additional water added to the carbon at the ends of the tube. Figure 16 is a photograph of a high yield area of exp. 80. Silicic acid was not mixed with the reactants in this boat. A function of the silicic acid intimately mixed with the reactants different from the initial reason for addition was not discovered.

c. Characterization of NM Filaments

The NM whiskers produced ranged in size from those small enough to undergo brownian motion to those growing on the surface of the carbon which were often 5mm long. Those produced in experiments paralled exp. 69 were mostly 10 to 40 μ long, and 0.5 to 1 μ in diameter. These filaments appear to be round, but this was not verified.

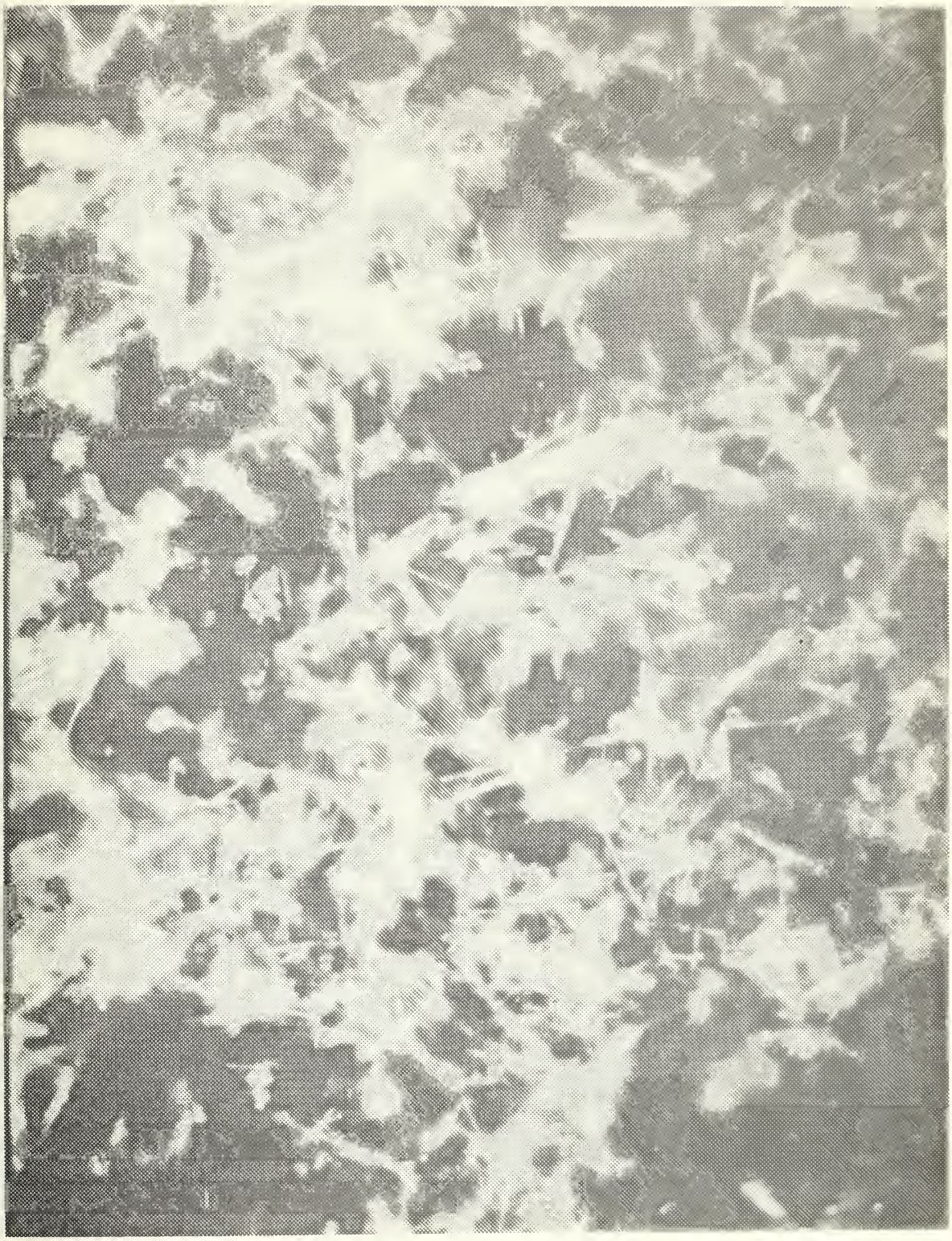

Figure 12. Clear, non-magnetic filaments produced in abundance in exp. 69. This is a typical example of yield and distribution. Magnifications 160X, enlargement 6.4X. (1024X)

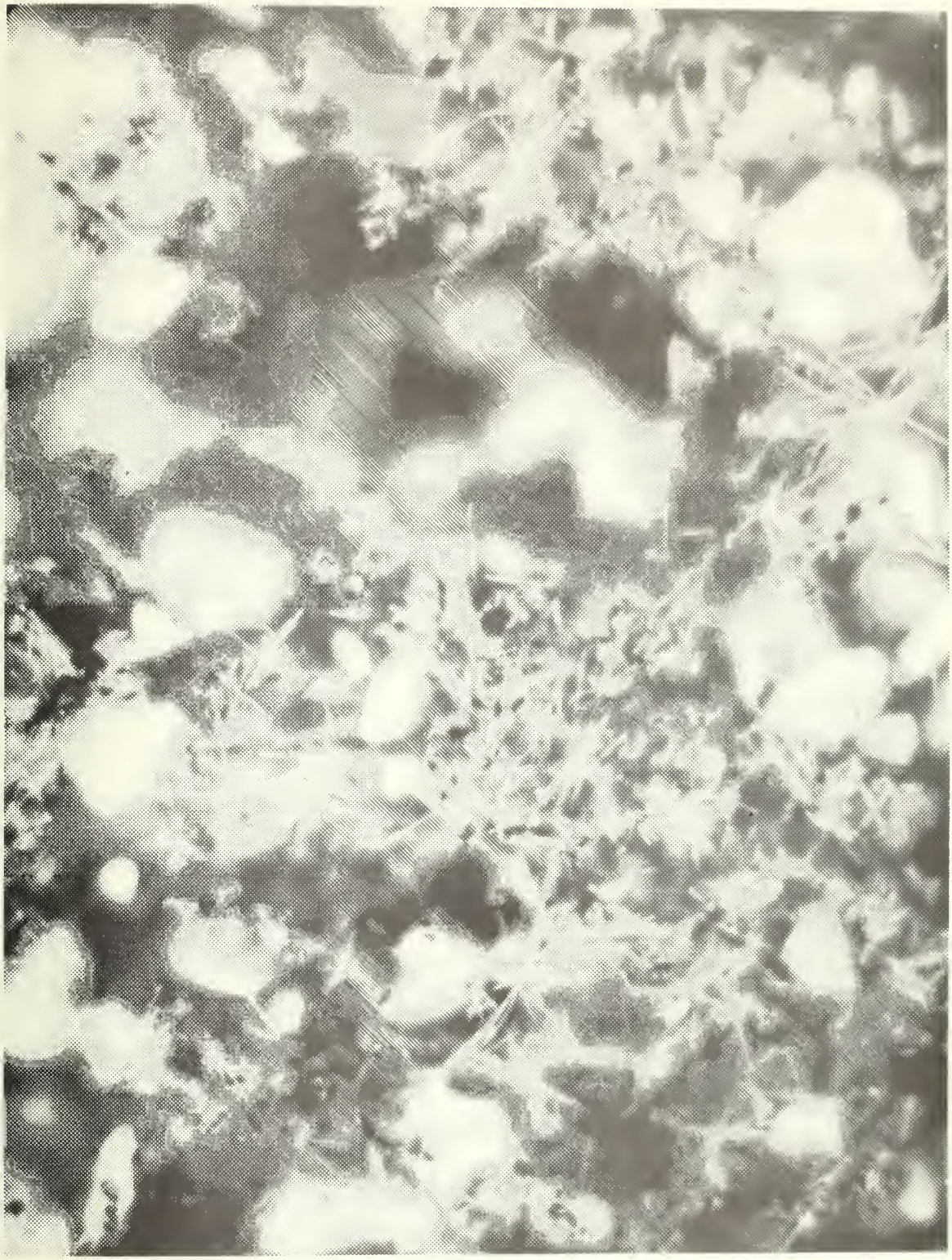

Figure 13. Concentration of filaments produced in exp. 82. Magnification 160X, enlargement 6.4X. (1024X)

Many of the filaments were freed from the carbon on which they grew by the addition of water. Separation was attempted using the expected density differences between the carbon, SiO_2, and the NM filaments. The matrix from experiment 87 was washed in about 400 ml H_2O and filtered to remove any soluble halide and the solids were air dried. Diiodomethane (CH_2I_2, ρ=3.3) was mixed with benzene (ρ=.879) to produce different densities. It was found that the matrix reacted as though it were of one density (calculated at ρ=3.03) and no separation resulted.

A crystal powder pattern was made of a sample of the three component matrix as produced by exp. 69. The peaks produced were many and very broad. No concrete assignment could be made from this data, however, ferrous phosphate, $Fe_3(PO_4)_2$, remained as probable.

The production of NM filaments required only the presence of $Ca_3(PO_4)_2$ and $FeCl_2$ as evidenced by exps. 70 and 71. Production was also possible if $FeBr_2$ was used with bone charcoal. Filaments also resulted when a non-reducing helium atmosphere was used, as in exps. 66 and 71. Figure 14 is a photograph of the non-filamentary crystals produced in exp. 71 which in every way resembled crystals often found in the carbon matrix of other experiments, particularly if the yield was poor.

The NM filaments are possibly the product of a cation exchange reaction between the iron halide and the calcium phosphate. The material could range from $Fe_3(PO_4)_2$ to numerous mixed salt possibilities.

d. The Growth Mechanism of NM Filaments

NM filaments bear some resemblance to those which grow by the VLS mechanism. As can bee seen from figures 15 - 19, these filaments generally have balls at the tip. They also usually have unexplained globules attached to their sides. They do not appear to be

Figure 14. Clumps of short, chunky, transparent crystals produced in exp. 71. Magnification 200X, enlargement 6.4X. (1280X)

Figure 15. Shiny, bright whiskers from exp. 65 remaining after matrix boiled in water to remove soluble halide and the residue treated with .1 M HCl for 10 minutes. Magnification 160X, enlargement 6.4X. (1024X)

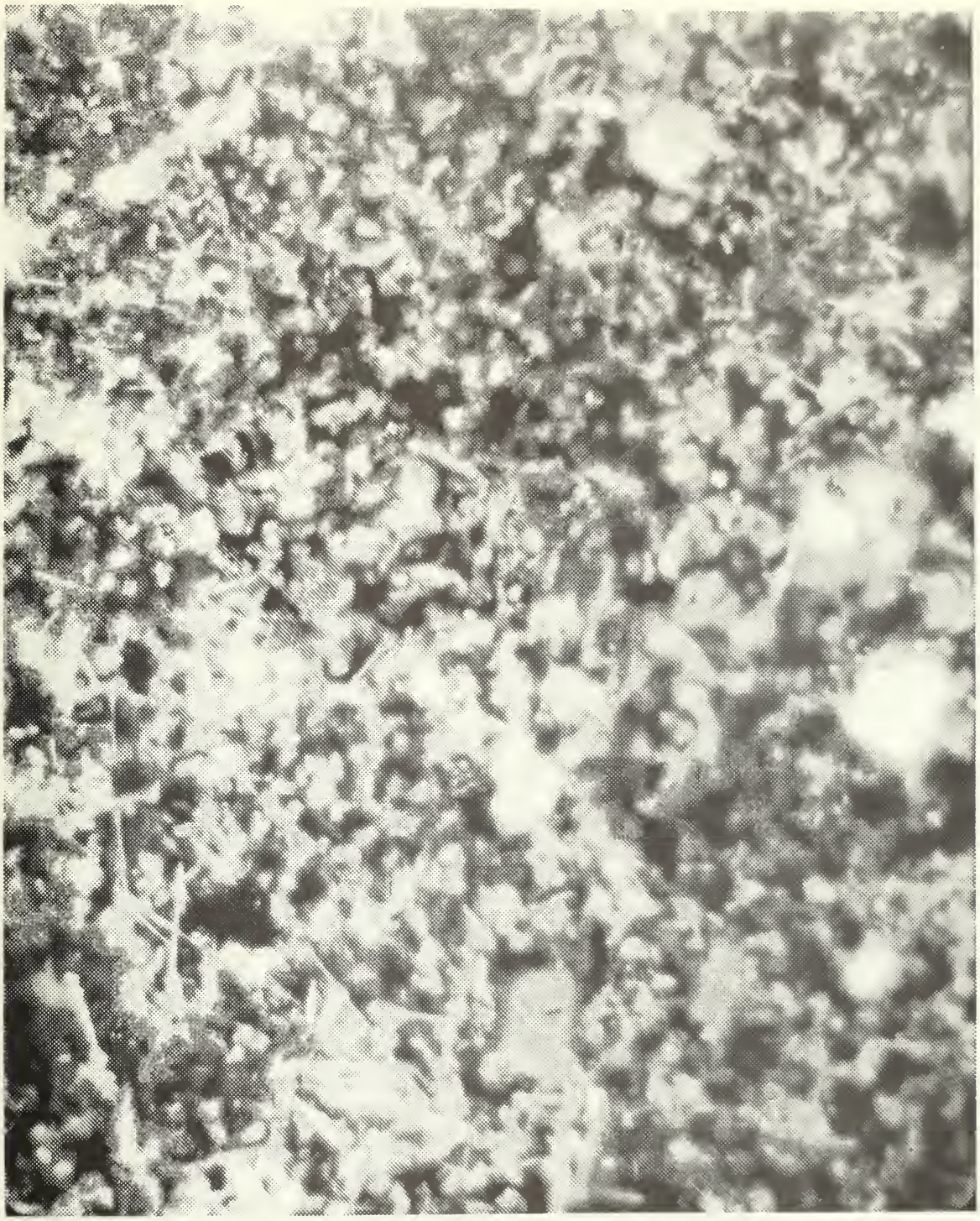

Figure 16. Good yield area of poor, spotty yield produced in exp. 80. Magnification 160X, enlargement 6.4X. (1024X)

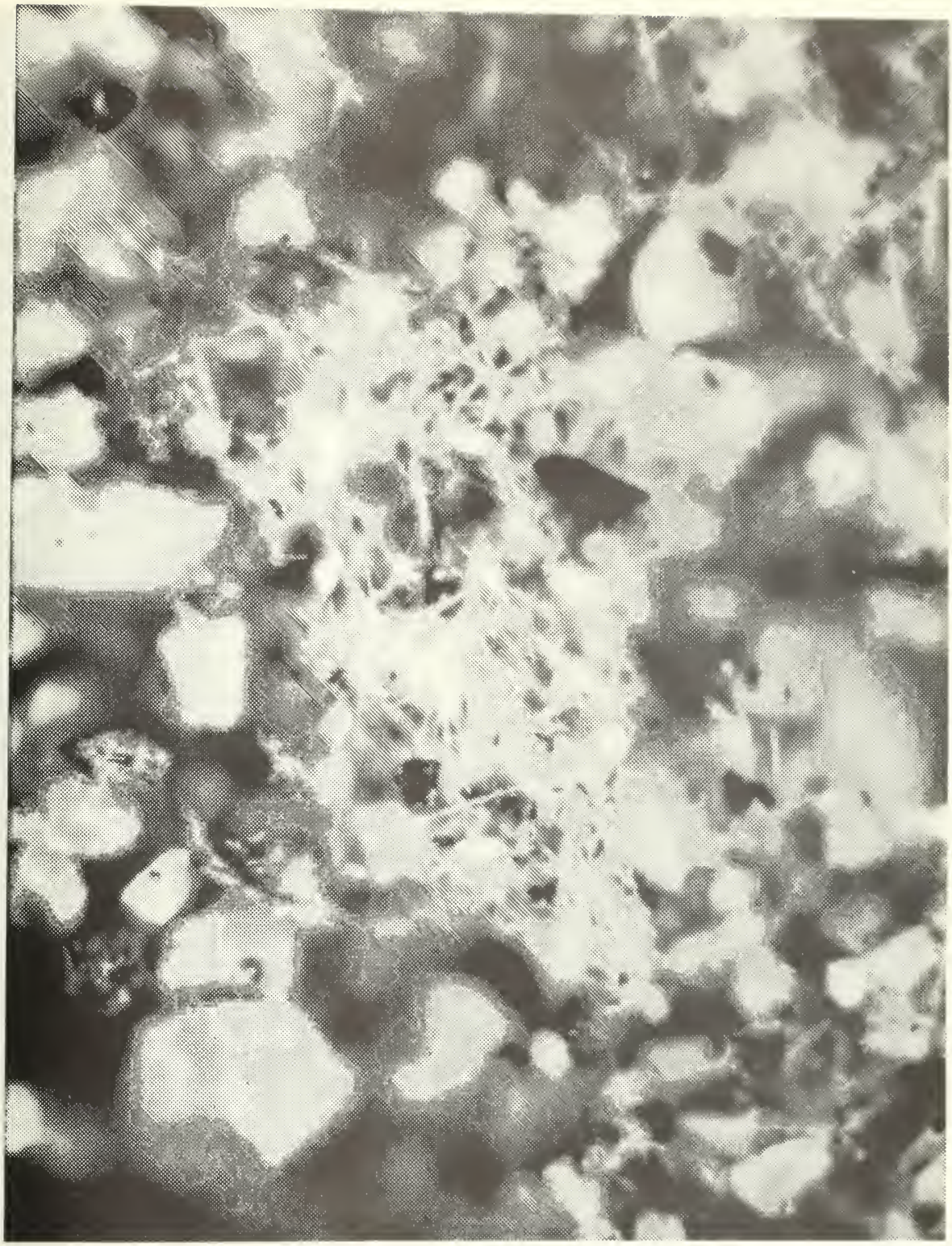

Figure 17. High yield, white area of exp. 81. Magnification 160X, enlargement 6.4X. (1024X)

Figure 18. Cluster of white filaments from a single base. Each spike has a bulb at its tip. Exp. 65. Magnification 640X, enlargement 6.4X. (4096X)

Figure 19. Single whisker with a red bulb at tip isolated in matrix of exp. 65. Note straightness, beads adhering to stem and shape of ball at tip. Magnification 400X, enlargement 6.4X. (2560X)

strongly attached to the substrate on which they grow. Figure 18 shows a cluster of NM filaments produced in exp. 65. The unusual formation apparently shows many filaments growing from the parent material. This is similar to the growth produced with silicon when the liquid bubble cap required for the VLS mechanism splits into smaller bulbs as depicted in Ref. 9. Figure 19 shows a single whisker also produced in exp. 65. This filament had a bulb which was bromine red in color. The globules attached to the stem are clear. In overall appearance this filament and the ones in Figures 9 and 10 are very similar.

e. Conclusions

The NM whiskers are a salt. The growth technique has some of the appearances of being a VLS mechanism, however, the transport of a phosphate salt in the vapor phase appears remote as the phosphate salts of calcium and iron are not volatile and a reducing atmosphere does not appear necessary.

Liquid transport of dissolved material to the tip is an alternative. The globules seen attached to the whisker stem may have been the result of this liquid transport. The liquid ferrous halide may dissolve the calcium phosphate to provide the liquid.

Not enough is known about the system or the product to formulate a growth mechanism or even to choose between the two possible methods of material transport.

E. EXPERIMENTS WITH $FeCl_2 \cdot 4H_2O$ AND Fe_2O_3 MIXTURES

1. General

The reduction of reagent grade $FeCl_2 \cdot 4H_2O$ was observed to produce few filaments. This observation was also made by Gorsuch [Ref. 4]. No filaments are reported if the commercially available ferrous chloride is further purified. The impurity found most effective in stimulating whisker growth has been ferric oxide, Fe_2O_3. An 80:20, $FeCl_2 \cdot 4H_2O$:Fe_2O_3, mixture by weight was determined to be appropriate for most of the experiments conducted.

The mechanism by which the ferric oxide promotes whisker growth is not known. As noted earlier its presence in the melt not only promotes the growth of a greater number of whiskers but also affects the direction of crystal growth, i.e. ferric oxide causes growth of the [100] crystal face to produce whiskers of square cross-section. To a point ferric oxide also increases the number of whiskers and decreases their diameter as the percentage of oxide is increased.

2. General Experimental Observations

A brief account of experiments conducted using $FeCl_2 \cdot 4H_2O/Fe_2O_3$ mixtures is contained in Table III. All reductions were at 730°C in quartz boats with steel liners. Some general observations common to most experiments follow:

a. Most filaments grew at the edge of the liquid melt. If the melt reached surfaces other than the liner such as a piece of metal placed in the boat or the shank of a tack, growth occured at the melt line. The whiskers grew in the melt material and not on the liner or other foreign material. The whisker is attached to the foil upon completion of reduction and not to the liner or other substrate.

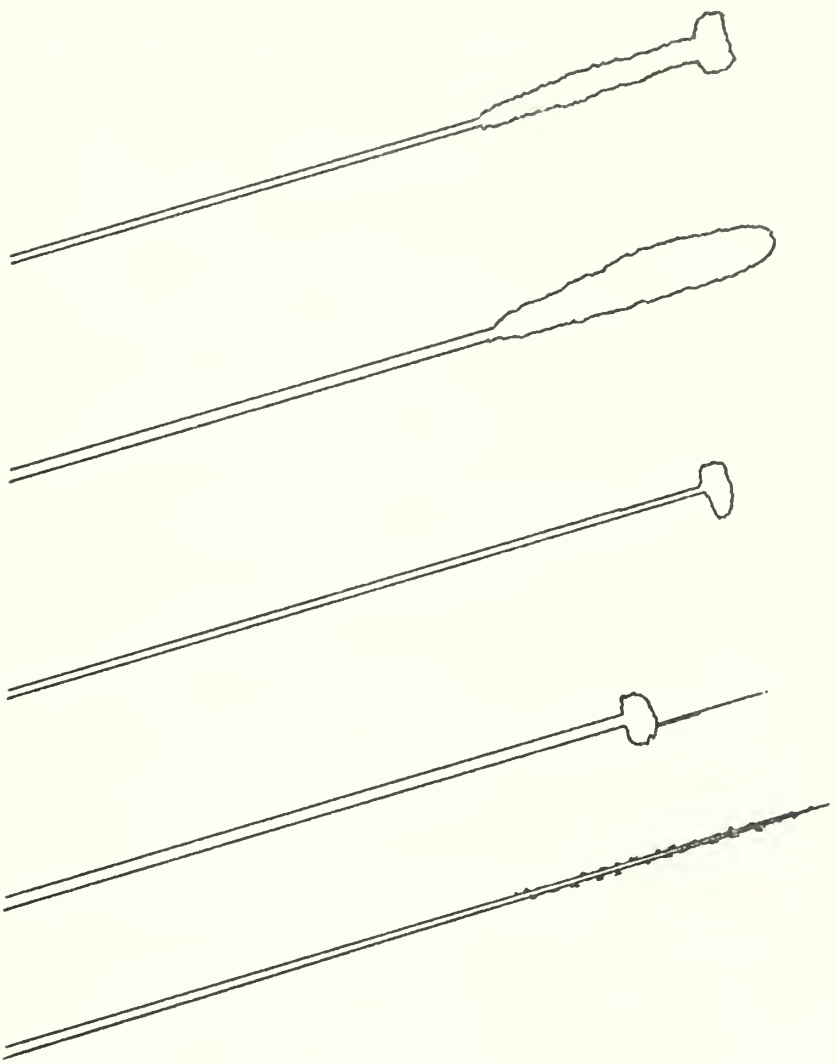

Figure 20. Typical Encrustations Observed at the Whisker Tips.

b. The vertical direction of whisker growth is generally limited to not more than 30^{o} above or 15^{o} below the horizontal. The longest whiskers generally grow horizontally at small angles above or below the horizontal. Whiskers appear to nucleate in all directions but only those with a growth path extending across the melt in areas of expected high supersaturation attain much length.

c. The tips of the whiskers are often encrusted with crystalline salt deposits. The bases of the whisker will not show any encrustation but as one examines the stem further from the base, crystalline deposits appear as a thin covering. This covering becomes much thicker near the whisker tip. Figure 20 is a drawing of some typical encrustation, and figure 5 is a picture of one such tip. Figure 8 is a picture of a slightly different physical form.

d. Some short filaments sometimes grew on the liner and quartz at the rear of the boat above the "water line." These whiskers were short, clean, crooked and tightly attached to the substrate. They grew in various directions and the cross sectional shape varied from whisker to whisker but could easily be determined visually. They were never long filaments.

e. With the aid of the stereo microscope the tips of whiskers grown in these experiments appeared to have a smaller diameter than their respective bases. This taper was common to all reactant mixtures though not all whiskers.

f. Clumps of whiskers growing at the "water line" from apparently the same point are very common.

3. Evaluation of Important Experiments

a. Reactants in the Early Stages of Growth

Experiments 96-107 examine the early stages of the reduction of both the pure reactants and a mixture. The Fe_2O_3 reduces to a grey solid in less than one minute. No further physical change was noted. $FeCl_2 \cdot 4H_2O$ melts in about 2½ minutes and no whiskers are present before 3 minutes. The 80:20 mixture of ferrous chloride/ferric oxide melted within 2 minutes and whiskers had formed after 2½ minutes.

b. Distribution of Fe_2O_3

In experiment 110 Fe_2O_3 was pressed on the bottom of the liner and $FeCl_2 \cdot 4H_2O$ spread above it. In experiment 112 $FeCl_2 \cdot 4H_2O$ was pressed on the bottom of the liner and Fe_2O_3 spread above. The resultant yields were very similar indicating either Fe_2O_3 is soluble in molten $FeCl_2$ or the undissolved Fe_2O_3 particles are mobile.

c. Cupped Pin Boats

Many experiments, Table III, were conducted using cupped pins. The reason was to determine if Fe_2O_3 placed a distance from the melt (in the cup of the pin) would be a preferential nucleation site. $FeCl_2 \cdot 4H_2O$ and $FeCl_2 \cdot 4H_2O/Fe_2O_3$ mixes were also tried to determine if growth once started would continue by receiving vapor or even liquid from the main melt. The results, though inconclusive, indicated that neither nucleation nor started filaments resulted at the cups. Figure 21 is a diagram of a cupped pin. Alteration of the cup size or other procedures might be employed to check this result.

d. Flat-topped Pins

Flat-topped pins were used to determine what effect if any the height of the pin had on whisker nucleation. Tall pins had growth

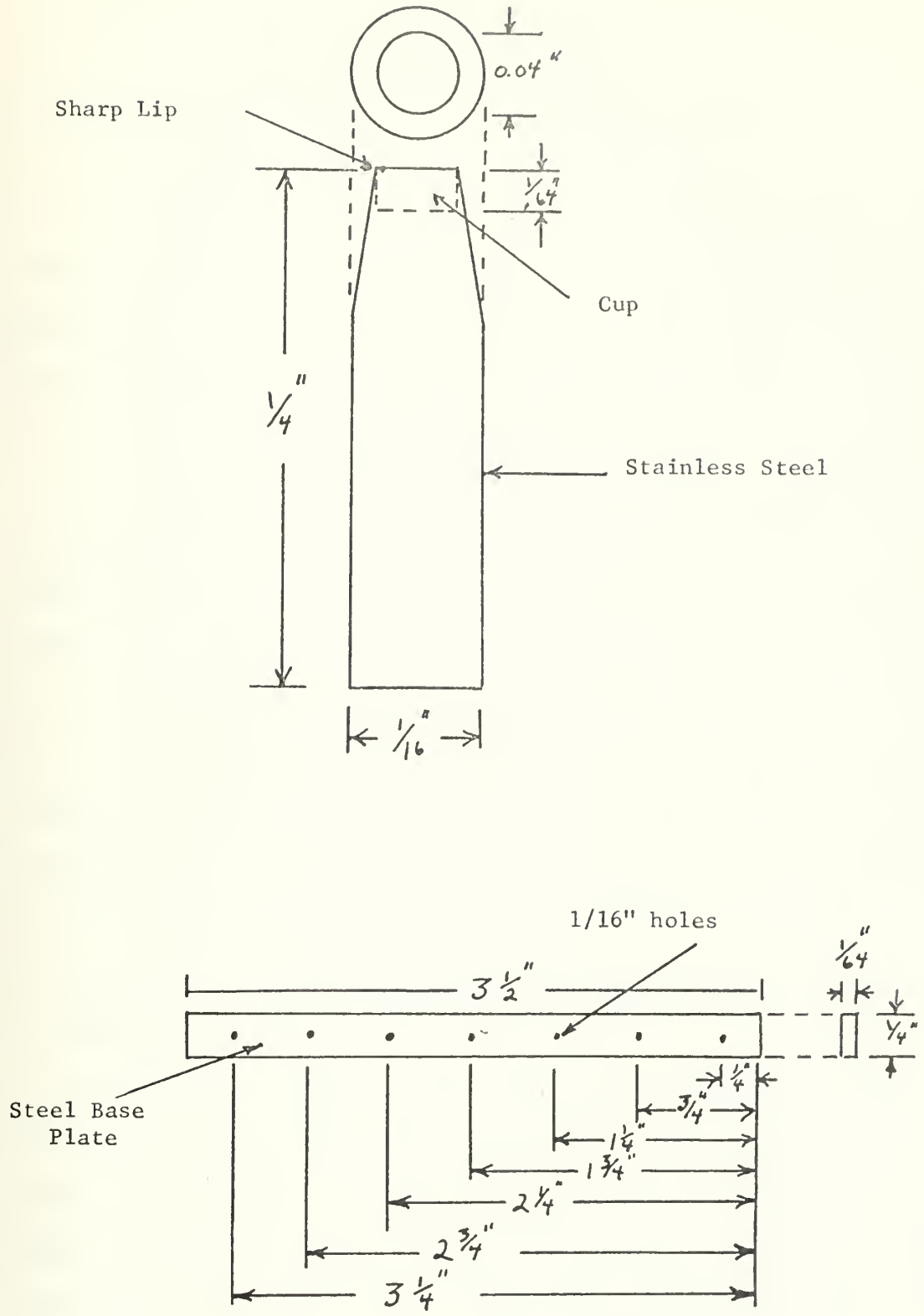

Figure 21. Schematic of Cupped Pin and Base Plate. Drawing is not to Scale.

at the edge of the melt. Pins short enough to be under the melt did not grow whiskers. Pins exactly the correct height had whiskers growing on the top as well as the sides. No preferential growth was observed.

e. Old Pins

Several experiments with old pins, experiments 128-129, produced preferential nucleation. Attempts to repeat the procedure and reproduce the results failed. Experiment 141 also produced and unexpected crop of filaments when yellow rust was present.

f. Covering Liners with Freshly Reduced Iron

One side of a liner was coated with freshly reduced iron by reducing $FeCl_2 \cdot 4H_2O$ in a tipped liner. The liner was then used to determine if preferential growth would result. No significant preference was found.

4. Conclusions

Iron oxide was determined to be required to achieve reasonable yields of whiskers. Very little was learned about the sometimes observed preferential nucleation. The function of Fe_2O_3 in the growth process was not discovered.

F. CORRELATION OF OBSERVATIONS ON GROWTH FROM A LIQUID MELT WITH PROPOSED MECHANISMS

Application of the three mechanisms cited in section II of this thesis to the observations made in the experiments conducted and to observations reported in the current literature lends support to the cold tip mechanism proposed by Hovermale [Ref. 7]. The addition of a few refinements supported by experimental observation make the explanation more than plausible. The possibility of whiskers growing by more than one mechanism in the same boat cannot be ignored. The major observations are

correlated below with the growth theories:

1. A salt-like covering was generally found at the tip. This had been noticed previously by Gorsuch [Ref. 4], who reported without a mechanistic explanation that many tips had crystalline growths of fantastic degrees of complexity. One would not expect to see the crystals formed when a monolayer of iron halide crystallized on the growth step of a whisker tip when the reaction vessel was removed from the hot zone. If the VLS mechanism were responsible one would expect to find crystals or a half round ball at the tip only and not clean bases and a gradual increase in the thickness of the crystalline encrustation of the stem until the tip is reached. If preferential halide condensation resulted at the thinnest part of the filament (the tip) due to its ability to reduce its surface temperature the fastest, one would expect the same covering distribution whether the reduction was actively in progress at the tip at the time of withdrawal or not. To investigate this experiments 119-125 were conducted (Table III). Two boats with the same amount of material were run. The first was reduced in the prescribed manner for 10 minutes. The second was reduced for 7 minutes with hydrogen and then the hydrogen flow was stopped and a helium flow started at the same rate. At the end of ten minutes this boat was removed from the heat. The boat which was still undergoing reduction when removed (hydrogen only for 10 minutes) contained whiskers which had clean, shiny bases and encrusted tips. The second boat had encrustations the entire length of the whisker. Figures 22 and 23 are pictures of the bases of whiskers in experiments 119 and 120. The results for the other experiments cited were similar. It is therefore concluded that the reaction and the encrustation pattern are not two separate entities but effect one another.

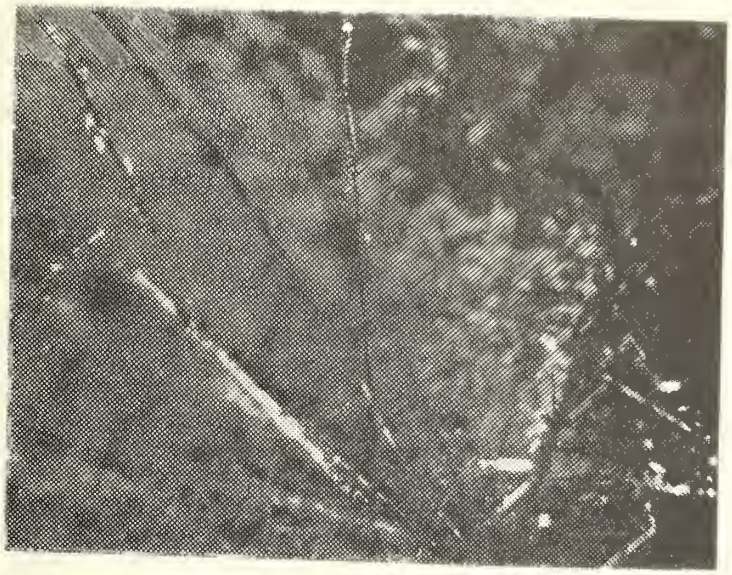

Figure 22. Base of whisker clump exhibiting clean bases and encrusted tips, exp. 119. Magnification 30X.

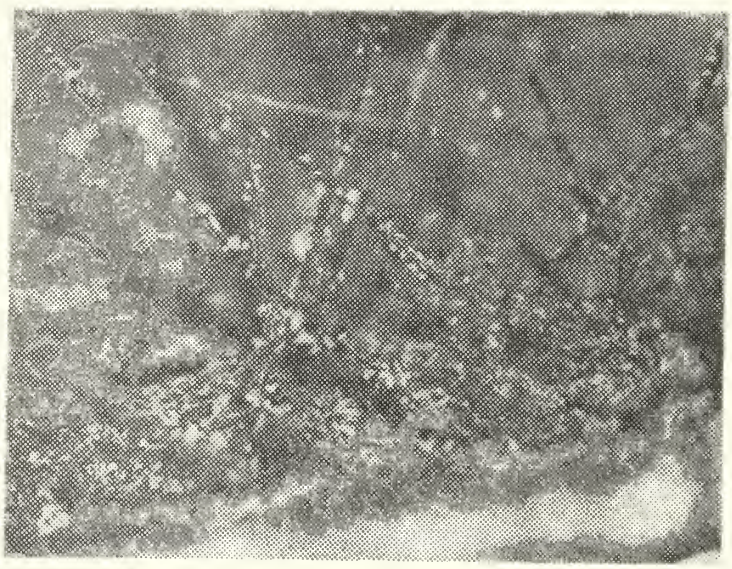

Figure 23. Base of whisker clump exhibiting encrusted bases and tips when He flow is substituted for H_2 flow three minutes prior to removal from furnace from exp. 120. Magnification 30 X.

2. Almost all whisker growth occured at the edge of the melt. The base of the whisker apparently must be in contact with molten halide. Gorsuch [Ref. 4] was able to watch the reduction as it proceeded. He witnessed whiskers growing from the surface of the liquid until the surface tension no longer would support their mass and they sank. Neither the screw dislocation theory nor the VLS mechanism require the whisker to be in contact with a liquid, however, virtually all filaments grown in the experiments conducted grew only where they had their base wet. Furthermore, if the formation of microcrystals are required to form a screw dislocation as proposed by Wokulska and Wokulski [Ref. 12], they would of necessity be required to form on the surface of the liquid to explain the experimental observations. Varying the substrate would also be presumed to have some effect if a screw dislocation mechanism were responsible for the predominant growth.

3. The presence of iron oxide would have a positive effect on whiskers grown by the screw dislocation mechanism only if it provided a site for microcrystal nucleation. Iron oxide could provide a nucleation site for whiskers growing by the cold tip mechanism or it could be a catalyst for either the cold tip or VLS mechanisms. The fact that the presence of iron oxide affects the crystal structure is an indication of an influence which is present in the initial stages of growth.

4. The rate of hydrogen flow would be expected to greatly influence growth by vapor transport of reactants to a growth step. Such transport is required by both the VLS and screw dislocation mechanisms. Experimentally, except at very high flow rates, it has little observed effect on the whisker growth.

5. The screw dislocation theory does not predict tapered whiskers since each layer is an exact duplicate of the preceding. Levitt [Ref. 9] has shown that the diameter of a VLS crystal is controlled by three factors; the initial amount of impurity, the deposition temperature, and the vapor-solid deposit which also depends on the deposition temperature. Therefore, for a given whisker, temperature change alone would be responsible for taper. In the experiments conducted by Levitt, increasing temperature increases the whisker diameter. Gorsuch [Ref. 4] has observed as temperature is increased, the amount of taper was radically increased. If similar mechanisms apply one would expect similar results. The diameter of a VLS grown whisker is controlled by the diameter of the liquid ball present. The amount of material present in the ball changes only slightly during VLS growth, however, temperature change affects the diameter of the eutectic ball. If liquid halide at the tip of a cold tip whisker also assumes a ball or toroid shape as indicated by examination of the salt deposits on whisker tips the amount of material available in the ball would be expected to decrease as the whisker grew due to reduced liquid flow caused by the greater length of travel required for the liquid to reach the tip. At higher temperatures it can also be assumed that the increased evaporation rate of halide from the whisker surface will affect the amount of halide reaching the tip in such a way as to reduce the flow. As the whisker grows a more rapid decrease in the diameter of the ball with length extension would occur resulting in a more tapered whisker.

Taper might also be totally or partially the result of the accretion of material on the sides of the stem. Neither the screw dislocation mechanism or the VLS mechanism provides for the addition of material at any point but the tip.

6. None of the three theories predicts preferential growth direction with respect to the boat geometry, however, all three depend on the tip being in the presence of a supersaturated halide vapor. The more supersaturated the vapor, the faster the deposition of material at the growth site. The greatest growth extension would be predicted in the areas of highest supersaturation, i.e. over the center of the melt and close to its surface which was in fact observed. Nucleation in all directions with continued growth in only a limited area is indicative of a mechanism dependent on the presence of vapor phase reactants in some way. The function could be to maintain a liquid on the surface by reducing the evaporation rate as well as providing material for reduction.

7. The small, short, clean whiskers growing at the down stream end of the quartz boat and on the after parts of the liner above the melt did not grow in contact with liquid halide. The whisker material was of necessity transported in vapor form. The hydrogen atmosphere at this point in the boat would be well saturated with halide having passed over the bulk of the melt. Since a foil is deposited on the quartz and iron surfaces where these whiskers grow, ample opportunity exists for the production of microcrystals and the screw dislocations associated with them. The growth of these short whiskers is probably the result of the screw dislocation technique and the initial iron (foil) deposit the result of surface catalyzed reduction.

Copper whiskers are similar in their growth characteristics to iron whiskers. Hasigui [Ref. 6] discovered the existence of axial screw dislocations in the secondary whiskers of copper produced by halide reduction. The absence of dislocations in primary whiskers is indicative of two separate mechanisms functioning under similar conditions. The

primary whiskers grew by a mechanism such as the cold tip which does not require a dislocation. When liquid halide no longer covers the sides of the whiskers nucleation of microcrystals can occur which produce screw dislocations and the associated secondary growth.

G. PROPOSED ADDITION TO COLD TIP THEORY

The observations made from the experiments conducted can best be rationalized with the cold tip theory. However, these observations suggest additional proposals.

The cold tip theory presented by Hovermale [Ref. 7] does not specify a physical shape, if any, to be assumed by the liquid when it reaches the tip. No reason has been given to explain either preferential reduction or deposition at the tip or to explain the reduction of all the liquid which flows there. The method by which extension in one direction proceeds at a greater rate than in any other growth direction is also ignored.

Observations made of the crystalline forms at the whisker tips indicate that the liquid probably forms a ball or toroid shape at the tip. Since the reaction does not proceed to any appreciable extent in the gas phase the rate of reaction can be assumed to be a function of the surface area of the liquid. If one assumes the liquid forms a small sphere with a diameter equal to twice the length of one of the sides of a whisker of square cross section the increased surface area is 11.57 times that of the whisker tip. For larger relative diamenter the increase in surface area is a function of the square of the diameter. The small area available for deposition combined with the large exposed surface area would ensure more rapid extension at the tip than elsewhere. The larger

the liquid bubble relative to the whisker diameter the more rapid would be the growth.

Since the cold tip theory does not require a growth step, reduction proceeding in the liquid as it flows up the whisker stem would result in deposition on the crystal surface. This deposition would tend to increase or create taper as the whisker grows. This does not eliminate the possibility that the diameter of the leader growth at the tip is partially controlled by the amount of material, size of the liquid bulb at the tip.

IV. CONCLUSION

A. SUMMARY

The observations made in the experiments conducted lend strong support to the cold tip theory. Neither the VLS nor the screw dislocation theories can be rationalized to adequately explain the observations made for growth at the edge of the melt. While the VLS mechanism can to some extent explain the presence of a crystalline substance at the tip its ordered presence below the tip remains unexplained. From the thermodynamics involved reduction in either the gas phase or requiring condensation at the reaction site would produce a "hot tip" which would oppose the flow of material from the gas phase and the presence of any liquid at the tip.

The screw dislocation mechanism is well founded on a theoretical basis. The bulk of the observations concerning whisker growth at the edge of the melt does not support this mechanism. Whiskers which are observed to grow above the melt edge can be explained by this theory. The existence of more than one growth mechanism for the reduction of iron halides is probably the reason very different observations have been obtained by researchers in the field. Observations supporting a screw dislocation were based on experimental methods which produced whiskers primarily by this method, i.e. generally only the vapor came in contact with the substrate. Experimental observations refuting the mechanism were based on growth involving whiskers in contact with the melt. Ambiguous observations resulted from experiments where both mechanisms functioned.

The cold tip theory provides a rational mechanism to explain the physical structure and appearance of whiskers grown at the edge of the melt. The change in the pattern of salt encrustation on the whisker stems noted when helium was introduced prior to removal of the sample (exps. 119-125, Table III) may be explained assuming that the He stopped the reaction, allowing equilibration of temperature differences. Neither the forces which provide the flow of liquid reactants or the nucleation process are understood though there is strong experimental evidence linking nucleation and/or early growth with ferric oxide as a catalyst remains as a possibility.

A complete theoretical model of the cold tip mechanism of whisker growth will involve not only reaction thermodynamics and heat flow but also surface adsorption phenomenon, the kinetics of two phase reactions and fluid dynamics. The proposal does, however, provide a basis from which to build a theoretical model. This model and/or experiments designed to exploit the proposed principles of growth may result in the future method of production of useable iron whiskers.

The non-magnetic whiskers produced in these experiments are unique for their large yield and ease of separation from the substrate. The physical characteristics of the grown whiskers indicate that they grow by a mechanism similar to the proposed cold tip, i.e. they possess bulbs at the tip and globules are attached to the sides. The possible uses of these crystals will not be known until they have been identified and their physical properties determined.

B. SUGGESTIONS FOR FURTHER ANALYSIS

Though the presence of liquid flowing up the sides of the whisker has been presented as very probable the fact remains unproven. The possibility

exists that careful visual examination of whiskers as they grow will enable the observer to determine if the surface of the whisker is wet and if indeed a flow of liquid up the stem exists. The visual observation of liquid halide at the tip and its shape would have equally important mechanistic implications.

The function of iron oxide is critical to understanding the complete mechanism. Radioactive isotopes of iron as Fe_2O_3 might provide the information required to determine the site at which it functions. Whiskers grown using radioactive isotope could be analysed at different points (areas) of the whisker (tip, base, middle) to determine the locations of isotope concentrations, if any. The possibility of exchange reactions may severely limit this procedure and should be carefully checked before embarking on elaborate experiments.

The identification and characterization of the non-magnetic filaments produced by the high temperature fusing of an iron halide and calcium orthophosphate also bears further investigation.

APPENDIX A

LIST OF CHEMICALS USED

Acid Silicic - 100 mesh powder - $SiO_2 \cdot X\ H_2O$ - Analytical Reagent
Manufacturer: 5

Ammonium Bromide - granular - NH_4Br - F.W. 97.95 - Reagent Grade
Manufacturer: 1

Charcoal - bone
Manufacturer: 5

Charcoal - cocoanut, activated - 6-14 mesh
Manufacturer: 6

Charcoal - "DARCO," activated - 20-40 mesh
Manufacturer: 2

Charcoal - "NORIT A," activated powder
Manufacturer: 2

Ferric Chloride - lump - $FeCl_3 \cdot 6H_2O$ - F.W. 270.32 - Reagent Grade
Manufacturer: 4

Ferric Oxide - Powder - Fe_2O_3 - F.W. 159.69 - Reagent Grade
Manufacturer: 4

Ferrous Bromide - hydrated
Manufacturer: 7

Ferrous Chloride - $FeCl_2 \cdot 4H_2O$ - F.W. 198.81 - Reagent Grade
Manufacturer: 4

Graphite - Powder - Grade 38
Manufacturer: 3

Lamp Black - Germantown
Manufacturer: 8

Manufacturers

1. Allied Chemical
   Specialty Chemicals Division
   Morristown, N.J.

2. Analabs Incorporated
   80 Republic Drive
   North Haven, Conn.

3. Fisher Scientific Co.
   Fair Lawn, N.J.

4. J. T. Baker Chemical Co.
   Philipsburg, N.J.

5. Mallinckrodt Chemical Works
   St. Louis, Mo.

6. Matheson, Coleman & Bell
   Norwood, Ohio

7. Research Chemical Corp.
   11686 Sheldon St.
   Sun Valley, Calif.

8. Sargent-Welch Scientific Co.
   7300 North Linden Ave.
   Skokie, Ill.

TABLE I. EXPERIMENTS CONDUCTED WITH 7:11 MIX AND CARBON

T = 730°C. H_2 flow rate = 0.3 ft^3/hr (CFH). 7:11 mix = weight ratio mix of Fe_2O_3 to NH_4Br.

Exp. #	Type and wt. of carbon	7:11 Mix grams	Red. time minutes	Observations
25	.2g NORIT A	2.5	10	Some very small whiskers
26	.16g NORIT A	2.0	10	Foil, many very fine whiskers, bulb at tip (metallic)
27	.12g NORIT A	2.0	10	Foil covers bottom of boat, not many whiskers. Tips have yellowish covering or metallic clusters.
28	.06g NORIT A	1.0	8	½ spilled out - fuzzy, fluffy matrix above foil
29	.5g Bone Charcoal	1.5	11	Some very small whiskers
30	1.5g Bone Charcoal	2.0	10	Great mass of small tangled whiskers in interior of matrix
31	1.5g Bone Charcoal	1.5	10	Great mass of tangled, tiny whiskers in interior of matrix
32	2.0g Bone Charcoal	1.0	10	Whiskers inside soft powder-like matrix
33	2.0g Bone Charcoal	0.5	10	Few whiskers, reduced foil
35	1.1g Bone Charcoal	1.1	7	Yellow salt covering whiskers - balls seen at ends
36	1.1g Bone Charcoal	1.1	6	No change from exp. 35
37	1.1g Bone Charcoal	1.1	5	No change from exp. 35
38	1.1g Bone Charcoal	1.1	4	Thick yellow bumpy structures which resemble well padded filaments have replaced the whiskers. Clusters of clean, shiny whiskers with balls at one end appear in clusters

Exp. #	Type and wt. of carbon	7:11 Mix grams	Red. time minutes	Observations
39	1.1g Bone Charcoal	1.1	3	Filaments covered with white or clear bumpy covering which dissolves in H_2O. Filaments are branched and bent
40	1.1g Bone Charcoal	1.1	2	Same as exp. 39 except less covering
41	1.1g Bone Charcoal	1.1	1	Very fine distorted filaments, some unreduced Fe_2O_3
42	1.1g Bone Charcoal	1.1	½	Same as starting material
43	1.1g Bone Charcoal	1.1	$\frac{3}{4}$	Same as exp. 42 except for some tiny filaments which grow in close proximity to each other
46	1.0g Bone Charcoal	1.0	10	Fe_2O_3 mixed with bone charcoal then NH_4Br added-- Larger percentage of straight whiskers. All had yellow crystals near tip end
48	1.0g Bone Charcoal	1.0	10	Reactants ground together resulting in dark red color. Whiskers formed were judged the same as unground mixture
49	1.2g Bone Charcoal	0.8	10	Same as exp. 48
50	1.6g Bone Charcoal	0.4	10	Very few whiskers-wet matrix shows shiny "buds" on carbon
51	1.8g Bone Charcoal	0.2	10	No whiskers visible while dry - wet matrix shows carbon covered with silver "dots." Dots appear to be balls of salt-like material when dry
53	1.8g Lamp Black	0.6	10	Whiskers in matrix were clumped, tangled and bent

TABLE II. EXPERIMENTS CONDUCTED TO PRODUCE NON-MAGNETIC, NM, WHISKERS.

T = 730°C H_2 and He flow rate = 0.3 ft^3/hr (CFH)

Exp.#	Reactants	Method	Observations and Comments
47	2g 7:11 mix, 2g bone charcoal	V 10 min.	Thin white covering appears on surface of carbon - very small filaments free in H_2O and undergo brownian motion.
54	2g 7:11 mix, 2g bone charcoal	V 10 min.	White covering on carbon and filaments - same as exp. 47.
55	.5g $FeCl_2 \cdot 4H_2O$, 2g bone charcoal	V 12 min.	Small clustered and branched whiskers encrusted with yellow covering. No small detached filaments produced.
56	.5g $FeBr_2$, 1g bone charcoal	V 10 min.	Carbon frosted but no free filaments produced when water added - a few filaments visible.
58	2g 7:11 mix, 1g lamp black	V 10 min.	No filaments present, no particles appear in water.
59	2g 7:11 mix, 1g NORIT A	V 10 min.	Frost on carbon but no filaments produced.
60	2g 7:11 mix, 1g graphite	V 10 min.	Some foil but no free filaments.
61	.6g $FeBr_2$, .6g NH_4Br, 1g bone charcoal	MH 10 min.	Many extremely fine, straight, long NM filaments. Are so thin as to be barely visible under high magnification.

V = Vapor Method - carbon placed in boat down stream of other reactants during hydrogen reduction.

MH= Mixture, hydrogen atmosphere - mixture reduced in flowing hydrogen atmosphere.

MHe=Mixture, helium atmosphere - mixture heated in flowing helium atmosphere.

Exp.#	Reactants	Method	Observations and Comments
62	.5g $FeBr_2$, .5g NH_4Br, 1g NORIT A	MH 10 min.	No filaments, some foil.
63	.5g $FeBr_2$, .5g NH_4Br, 1g lamp black	MH 10 min.	No filaments.
64	.5g $FeBr_2$, .5g NH_4Br, 1g graphite	MH 10 min.	No filaments.
65	1g $FeBr_2$, 1g NH_4Br, 1g bone charcoal	MH 10 min.	Many NM filaments, some branched, most straight. The addition of water produced a fair number of floating particles with attached filaments. Detached filaments do not respond to magnetic field but iron coated carbon particles do.
66	.5g $FeBr_2$, .5g NH_4Br 1g bone charcoal	MHe 1.5 hrs.	Reactants heated for one hour - lots of small filaments present. Addition of H_2O produces many straight filaments undergoing brownian motion. None react to an applied magnetic field.
69	2g $FeCl_2$, 2.5g bone charcoal, .5g Silicic acid	IT 15.5 hrs.	Matrix is solid with clear, NM filaments; many freed from carbon by water addition. Filaments are generally larger than previously produced and few exhibit brownian motion.
70	.3g $Ca_3(PO_4)_2$, 16g $FeCl_2$, 1g bone charcoal	IT 15.5 hrs.	Low number of NM filaments.
	.3g $Ca_3(PO_4)_2$, .6g $FeCl_2$, 1g lamp black		Fair number of NM filaments - matrix is very solid.
	.3g $Ca_3(PO_4)_2$, .1g $FeCl_2$, 1g NORIT A		Fair number of NM filaments.
	.5g $Ca_3(PO_4)_2$, 1g $FeCl_2$		Fair number of NM filaments.

IT = Iron Tube Method - reactants placed in boat which is placed in an iron tube with loose fitting plugs. Carbon is placed at both ends of the tube to provide a reducing atmosphere. The tube is slid inside the quartz tube which remains open to the atmosphere.

Exp.#	Reactants	Method	Observations and Comments
71	2g $FeCl_2$, .5g $Ca_3(PO_4)_2$	MHe 18.5 hrs.	A few large filaments, remaining material was clumps of short, chunky crystals.
72	2g $FeCl_2$, 2g bone charcoal	IT 19.5 hrs.	Some whiskers present but most of the crystals short and chunky as seen in exp. 71.
78	1g $Ca_3(PO_4)_2$, 1g $FeCl_2$, 1.5g bone charcoal	MH 25 min.	Fair number of whiskers on surface, fair yield in matrix.
79	1g $FeCl_2$, .5g $Ca_3(PO_4)_2$, 1.5g bone charcoal	MH 10 min.	Spotty yield; either lots of filaments or no filaments. Areas without filaments appear to contain reduced Fe. No free filaments in water.
80	2g $FeCl_2$, 2g bone charcoal	IT 16.5 hrs.	Spotty yield ranging from very good to poor.
81	2g $FeCl_2$, 2g matrix from exp. 80, .3g $Ca_3(PO_4)_2$	IT 5.5 hrs.	Surface of aft 1/3 of boat light to light grey with exceptional yield. The remainder of the boat had poor yield.
82	2g $FeCl_2$, 2g bone charcoal, .5g silicic acid	IT 17 hrs.	General yield good. Number of filaments present decreases with depth from surface. Matrix next to boat bottom contains none. Color of matrix changes from light grey at surface to dark grey at bottom of boat.
83	2g $FeCl_2$, .4g $Ca_3(PO_4)_2$, 1g silicic acid	IT 1 hr.	No filaments. The reactants remaining are friable and absorb water from the air.
84	2g $FeCl_3$, 2g. bone charcoal	IT 2.25 hrs.	Poor yield at surface - good yields inside - better toward bottom of boat.
86	2g $FeCl_3$, .2g $Ca_3(PO_4)_2$ 2g bone charcoal	IT 4.5 hrs.	Surface filaments appeared to be tangled, branched, fairly long metallic whiskers. Center of matrix contained a poor yield of both iron and NM filaments. The bottom of the boat contained a good yield of NM filaments.

Exp#	Reactants	Method	Observations and Comments
87	2g $FeCl_2$, 2g bone charcoal, .5g silicic acid	IT 2 hrs.	Good yield of NM filaments.
88	1.6g $FeCl_2$, .4g $Ca_3(PO_4)_2$, 2g lamp black	IT 16 hrs.	Few filaments - most of matrix appears as porous lumps - coke like.
90	2.5g $FeCl_3$, .5g $Ca_3(PO_4)_2$, 2g bone charcoal	IT 3.75 hrs.	Good yield. Ranges from poor at top to very good near bottom.

		H_2 flow (CFH)	
7	$FeCl_2$; $FeCl_3$	10 .4	$FeCl_2$ pressed into bottom of boat, $FeCl_3$ pressed on top. Crumbly, whiskerless mass resulted.
8	60:40 $FeCl_2$: $FeCl_3$	10 .25	A fair number of unremarkable whiskers grew at the edge of melt.
9	60:30:10 $FeCl_2$:$FeCl_3$: Fe_2O_3	10 .15	Fair number of whiskers. All heavily encrusted with unreduced salts.
10	60:30:10 $FeCl_2$:$FeCl_3$: Fe_2O_3	10 .15	NaF pressed into bottom of boat to provide soluble substrate. No whiskers.
11	80:20 $FeCl_2$:Fe_2O_3	10 .15	Fair growth of filaments, some very fine. Growth at edges of melt only.
12	60:40 $FeCl_2$:Fe_2O_3	5 .12	Some whiskers - foil like slag on bottom of the boat. Unreduced salts under foil and on some of the whiskers.
13	$FeCl_2$	10 .15	V boat used. Very few whiskers - reduced iron on bottom of boat.
14	60:30:10 $FeCl_2$: $FeCl_3$: Fe_2O_3	10 .15	V boat used. Fair number of whiskers. Encrustations less near bow of boat.
15	50:40:10 $FeCl_2$:$FeCl_3$: Fe_2O_3	10 .15	Fwd. section of boat pressed with spatula. Whisker growth in bow much thicker than remainder of boat - whisker yield fair - quality poor.

NOTE: Number ratios indicate mass ratios of respective reactants.

101	[illegible] Fe_2O_3	.3	reflecting surface broken by roads of black surface.

Exp.#	Reactants	Red. time (min) H_2 flow (CFH)	Procedure, Observation, Comments
103	1.5g 80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	2:30 .3	A few filaments formed at the edge of melt. Salts now form a smooth pool in the center of the boat.
105	1.5g 80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	3 .3	More filaments than exp. 103, all growing at edge of melt. Note: filaments grow in reactant material not on surface of liner near edge of reactant material.
106	1.5g 80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	4 .3	More filaments than exp. 105, all grow at edge, all have salt encrustations at tip. Growth is on outboard edge of "barrier mound."
107	1.5g 80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	5 .3	More filaments than exp. 106, some fairly long (1 cm) and growth is at edge of melt on out board side of "barrier mound."
108	1.5g 80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3 1.5g $FeCl_2 \cdot 4H_2O$	5 .3	Mixture placed in fwd. section of boat, homogeneous salt in after section. Piles melt together. A few whiskers produced in fwd. section, none aft. The melt edges of the two piles differed slightly.
110	1g Fe_2O_3; 2g $FeCl_2 \cdot 4H_2O$	10 .3	Fe_2O_3 pressed into bottom of boat and $FeCl_2 \cdot 4H_2O$ spread over top. Fair yield of poor quality whiskers located at edge of melt. Several different crystal types present.
111	2g $FeCl_2 \cdot 4H_2O$; .5g Fe_2O_3; Sprinkling of "DARCO" carbon	10 .3	Fair yield of poor quality whiskers. Most grow at edge of melt but some grow on higher lumps of carbon (foil covered). Encrustations on tips and sides. Single small amber torus or umbrella shaped globs surround some whiskers on the upper 2/3 of their length.
112	1g Fe_2O_3; 2g $FeCl_2 \cdot 4H_2O$	10 .3	$FeCl_2 \cdot 4H_2O$ pressed into bottom of boat and Fe_2O_3 placed above. Results same as exp. 110.

Exp.#	Reactants	Red. time (min) H_2 flow (CFH)	Procedure, Observation, Comments
113	2g $FeCl_2 \cdot 4H_2O$	10 .3	Small crop of filaments at edge of melt, heaviest amidships, more fwd. than aft. Some in fwd. section reveal four types of cross sections.
114	2g $FeCl_2 \cdot 4H_2O$; .5g Fe_2O_3	10 .3	Fair growth of whiskers, all thin, many branched, all tapered, all grow from edge of melt, some grow beam to beam.
115	2g $FeCl_2 \cdot 4H_2O$; .5g Fe_2O_3; .5g cocoanut charcoal	10	Lots of very poor, short, bent tangled whiskers rooted in foil.
116	1.5g $FeCl_2$ (anh.); .25g Fe_2O_3; 1.5g $FeCl_2$ (anh)	10 .3	$FeCl_2$ placed in fwd. portion of boat, mixture in after portion. Equal growth from both sections. Fair yield of poor quality, branched, bent and tapered whiskers. Salt covering visible on the filaments.
118	3.2g $FeCl_2 \cdot 4H_2O$; .8g Fe_2O_3	15 .3	Pin boat - 7 cupped 7 mm pins - cups 2, 4, and 6 contain mix - boat mix level about 2 mm below pin tips. Growth almost exclusively at height of melt. Few filaments near top of pin 5, 6, and 7, with bulbous tips.
119	1.6g $FeCl_2 \cdot 4H_2O$; .4g Fe_2O_3	10 .3	Very few filaments. Salt crusts almost exclusively at the filament tips. Some amber blobs are present. The lower ½ of each filament is shiny while the upper 3/4 had a salt covering which became denser toward the tip.
120	1.6g $FeCl_2 \cdot 4H_2O$; .4g Fe_2O_3	7 .3	At seven minutes H_2 flow was stopped and He flow of .3 CFH was started with the boat remaining in the furnace. Boat removed to cooling zone after 10 min. elapsed. Whiskers same as exp. 119 except heavy spotty encrustation present over entire length of whisker.

Exp.#	Reactants	Red. time (min) H_2 flow (CFH)	Procedure, Observation, Comments
121	2.0g $FeCl_2 \cdot 4H_2O$; .5g Fe_2O_3	10 .3	More filaments than exp. 119 where 2g of mix were used. No salt deposits appear at base of whiskers but do appear near tips.
122	2.0g $FeCl_2 \cdot 4H_2O$; .5g Fe_2O_3	7 .3	Same procedure as exp. 120. Low yield of whiskers. Salt deposits at tips and along sides less than exp. 120 although deposits exist from base to tip.
124	2.0g $FeCl_2 \cdot 4H_2O$; .5g Fe_2O_3	7 .3	Few whiskers, very little encrusted salt. Whiskers had shiny bases.
125	1.6g $FeCl_2 \cdot 4H_2O$; .4g Fe_2O_3	7 .3	Few whiskers. Very little encrusted salt. Whiskers had shiny bases and deposits at the tip.
126	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	10 .3	Two pin boat, 4.5 mm, aft cup contained mix. Mix height equals pin height. All growth on sides of pins, fwd. more than aft.
127	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	7 .3	Two pin boat, 3mm and 4mm, fwd. cup contained mix. Mix height slightly above pin height. Good growth on fwd. pin and a few short whiskers on after pin.
128	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	11 .3	Same as exp. 127 except the pins were previously used. Large yield of poor quality whiskers growing from the outside of the pins. The pins provided a preferential nucleation site.
129	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	11 .3	Same as exp. 128. Low yield of whiskers growing from liner. Large yield of whiskers growing from pins. Whiskers are of better quality than exp. 128. The pins provided a very preferential nucleation site.
130	$FeCl_2 \cdot 4H_2O$	12 .3	Same as exp. 127. Few stubby whiskers on liner and pins. More on pins than on liner.

Exp.#	Reactants	Red. time (min) H_2 flow (CFH)	Procedure, Observation, Comments
131	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	10 .3	Three pin boat using new cupped pins, height 4mm. Very few filaments.
132	$FeCl_2 \cdot 4H_2O$	10 .3	Same as exp. 131. Very few filaments.
134	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	10 .3	Three pin boat - same pins as exp. 131 except pin 3 replaced with new pin. Whiskers grew on outsides of pins at melt line and a few grew above the melt line. No preference for old pins noted.
135	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	10 .4	Boat coated with freshly reduced iron on one side only. Sparse yield on coated side, virtually none on uncoated side.
137	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	10 .3	Boat liner oxidized in furnace open to air. Oxidized liner black. Only a few very fine whiskers grew.
138	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	10 .4	Boat liner coated on one side with reduced Fe. Whiskers which grew were removed from fwd 2/3 of liner. Sparse yield of thin whiskers. Whiskers left from coating run became definitely thicker and had no salt crust.
139	$FeCl_2 \cdot 4H_2O$	12 .4	Six pin boat with used pins. Poor yield with more filaments fwd. than aft.
140	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	12 .4	Same as exp. 139. Few whiskers, most located on pins.
141	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	12 .4	Used liner, portion of liner covered with yellow rust. Good crop of filaments in area of yellow rust.
142	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	12 .6	Six pin boat of alternate tall (7mm) then short pins. Good growth on pins 1 and 6, very good growth on all other pins.

Exp.#	Reactants	Red. time (min) H_2 flow (CFH)	Procedure, Observation, Comments
143	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	12 .6	Same as exp. 142 except cupped pins filled with mix used. Growth ranged from no growth to very good growth with no pattern.
144	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	12 .6	Seven pin boat of alternate new then old pins. All but one pin had very good growth.
145	$FeCl_2 \cdot 4H_2O$	12 .6	Six pin boat of alternate short (4mm) then long (7mm) new pins. No whiskers grew on short pins which were under melt and few whiskers grew on long pins.
146	$FeCl_2 \cdot 4H_2O$	12 .6	Same as exp. 145 except pins are cupped. No whiskers on pins, few in boat.
147	$FeCl_2 \cdot 4H_2O$	10 .6	Same boat as exp. 139 cleaned and allowed to stand in air. Whiskers on pins 1,3,4,5 with the greatest number on pin 5. Few whiskers grow from the sides.
148	$FeCl_2 \cdot 4H_2O$	10 .6	Two different liners - one fresh - one allowed to air oxidize for three weeks. Both had indistinguishable small yields of fine whiskers.
149	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	10 .6	Same as exp. 148 except for reactants. Both liners had indistinguishable fair yields of fine whiskers.
150	80:20 $FeCl_2 \cdot 4H_2O$: Fe_2O_3	12 .6	Same as exp. 145. Fair crop of whiskers on pins. All growth is just above the height of the melt. No growth near top of the tall pins.
151	$FeCl_2 \cdot 4H_2O$	12 .6	1g Fe_2O_3 reduced for 8 minutes and $FeCl_2 \cdot 4H_2O$ added to the resulting black powder in the cooling zone. Growth similar to 80:20 mix.
152	$FeCl_2 \cdot 4H_2O$	15 .6	1g Fe_2O_3 reduced for 25 minutes and $FeCl_2 \cdot 4H_2O$ added to the grey powder in the cooling zone. No whisker growth.

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

ORIGINATING ACTIVITY (Corporate author)

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Monterey, California 93940

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

REPORT TITLE

The Growth of Iron Whiskers by the High Temperature Reduction of Ferrous Halide Salts.

DESCRIPTIVE NOTES (Type of report and, inclusive dates)

Master's Thesis; December 1972

AUTHOR(S) (First name, middle initial, last name)

Charles William Jaget

REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
December 1972	83	13

a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
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3. ABSTRACT

The growth mechanism of iron whiskers produced by the hydrogen reduction of iron halide salts was investigated by the variation of a number of parameters. The observations are correlated with current theories and with the thermodynamic behavior of this reaction which indicates that the tip of the growing whisker should be colder than the ambient medium (the cold tip). The mass growth of iron whiskers in the presence of carbon was examined to evaluate the potential of this method to produce marketable whiskers. An unidentified, non-metallic whisker growth was discovered growing in bone charcoal. Growth was determined to require the presence of a ferrous halide and calcium orthophosphate. Further postulates concerning the cool tip theory are made.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Crystal						
Whisker						
Cold tip theory						
Iron whiskers						
Non-magnetic filaments						

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The growth of iron whiskers by the high temperature reduction of ferrous halide salts.